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Improved Theoretical and Experimental Investigation of the Transient Hot-Wire Method for Measuring the Thermal Conductivity of Liquids, Especially of Its Applicability to Electrolytic Solutions

by

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Abstract

The transient hot-wire method is to-day widely used as a method for measuring the thermal conductivity of liquids. Its "classical" field of application is pure, dielectric liquids. The method is often claimed to be "elegant", fast, and convenient. It is therefore amazing that only a few attempts have till now been made at expanding it for measurements on electrolytic solutions.

That expansion is always carried out - or proposed carried out - in the literature by surrounding the hot wire with an electrically insulating layer. However, the layer gives rise to both practical and theoretical difficulties. E.g. Alas [1] (1967) used for theoretical reasons an extremely thin layer but he did not succeed in finding a material that is not dissolved by bases. [1] is therefore confined to aqueous salt solutions.

In [3] the present author presented a modification of the method in which the layer is avoided by altering the device so that the counter electromotive force from the electrolytical polarization is quickly made to bal-

ance with the voltage applied to the measuring cell. A naked hot wire can therefore be used, the electrolytic solution being barred from carrying electric current.

However, matters are not quite so simple as indicated, and an analysis is necessary to ensure that indeterminable sources of error do not occur. That analysis is to a certain degree given in [3], which builds upon a former work [2] by the same author in which certain sources of error of the method when it is applied to dielectric liquids were treated.

[2] and [3] contain the main points of the author's Ph.D. (lic. scient.) thesis, which appeared in Danish.

The present work is - together with [4] - an improvement of the investigations indicated above. In [4] the theory of the modification - which was in [3] rather limited - is discussed in every detail. In the present paper the experimental part of the work has been widened and [2], [3], and [4] are abstracted together with additions for making them quite up-to-date. The set-up was in [3] only developed to a semiautomatic stage and only 5 electrolytes were measured on in aqueous solutions of different concentrations in order to give experimental support to the modification. The accuracy was 1-1.5%. Now full automation has been introduced and 9 new electrolytes in different concentrations have been measured on - some of which are not found in the literature on λ measurements -. The accuracy turned out to be improved to 0.2-0.5% by the introduction of full automation. In total 76 individual electrolytic solutions have now been measured on at room temperature with the modified device, and every measurement on an individual solution is, in its turn, the mean of 10 or 5 determinations. The results are compared with values given in the literature and the agreement is found very satisfactory.

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lation material is dissolved by bases and his work is therefore confined to aqueous salt solutions. Furthermore, the coating must repeatedly be controlled for leakage. In the work [29] a thicker coating (a glass capillary tube) is used, but in 1953 van der Held had to revoke it (in collaboration with other researchers) [30].

In [29] van der Held et al. explicitly*) stated that it is impossible to use the naked wire in the solution. Nevertheless, the present author succeeded in doing so by modifying the measuring cell and the circuit so that

1) it is possible to operate below the decomposition voltage of a fairly comprehensive range of aqueous solutions of bases, acids and salts, and

2) the voltage applied to the measuring cell is made to balance quickly enough with the counter electromotive force from the electrolytic polarization. Owing to the last-mentioned circumstance the liquid column is barred from carrying electric current in a period large enough for measuring λ values without complications.

In [3] the author had only developed his modification to a semiautomatic stage and used it at that stage for confirming experimentally its soundness by measuring on some electrolytic solutions, the λ values of which are known from measurements by other methods and which are found in the literature. However, in section III of the present work is described the introduction of full automation which turned out to improve the accuracy essentially and - of course - to make routine series of measurements much easier.

In section III of the present work a more comprehensive set of measurements than those in [3] is therefore given. The main purpose of these measurements is still to give an experimental justification of the applicability of the modification but the author has also measured values which are not found in the data literature. E.g. λ for CsOH, LiOH, and NH_4OH solutions (at room temperature), which is either not found in the literature or not found in the concentration intervals used, is given. At any rate the author thinks that if these results have been published by other authors, they must be so new that the values measured are of interest for comparison. They are e.g. not found in the very comprehensive list of λ values for aqueous electrolytic solutions in Landoldt-Börnstein's tables, II Band, 5 Teil, 1968, which - as mentioned in section IV - may still be considered up-to-date.

*) The statement is quoted in [3], page 6.

The present work contains no statistical-thermodynamical discussion of the results. The purpose of the whole work has been to study the theory and practice of the measurement method - not to give a general discussion of energy transport in liquids or a detailed discussion of the agreement of measured values with theoretically predicted values.

Since no experimental work of the kind under discussion can be carried out without an underlying theory, the whole work has been widely guided by theoretical considerations. But as the author has been compelled to confine himself to studying only the theory of the measurement method, macroscopical non-equilibrium thermodynamics is deemed an adequate "tool". This seems to be in agreement with the treatment of different methods for λ measurement in the 2-volume composite work [28] from 1969 which may still be considered up-to-date and which shows how intensively the theory (and practice) of λ measurements by different methods are nowadays cultivated.

The theoretical basis of the author's work on the subject is the theory of the method in its original field of application, i.e. dielectric, pure liquids. As might be expected, one of the cornerstones of that theory is the problem of possible disturbances from convection. At the outset of the work it was surprising to see that convection in the measuring cells is, apparently without exceptions, treated by simply postulating or trying to prove *) that it is absent during the measurement period (usually about 10 second), cf. quotations in [2], page 14. Nevertheless, it is easy to see - both by observation and theoretically - that this is not so: in [2], page 16 is described the result of placing some light particles (earthmoss-seeds) in the liquid and switching on the current to the cell. (A small addition of a surface active agent was necessary to prevent the particles from clotting and ascending in the cell). Long before the expiry of the said measuring period lively convection was observed by means of a magnifying glass.

*) This is often done by considerations emphasizing the importance of the so-called 'Grashof-number'.

From a theoretical point of view it is also evident that mechanical equilibrium cannot exist simultaneously with a radial heat flow in the cells: let T, p and ρ be temperature, pressure and mass density of the pure liquid. The mechanical equilibrium condition then reads - using cartesian coordinates x, y, z with vertical z axis -

$$\frac{\partial p}{\partial x} = 0$$

$$\frac{\partial p}{\partial y} = 0$$

$$\frac{\partial p}{\partial z} = -\rho g$$

where g is the gravitational acceleration. Differentiating the first equation with respect to z and the last with respect to x one finds

$$\frac{\partial \rho}{\partial x} = 0 .$$

Analogously one has

$$\frac{\partial \rho}{\partial y} = 0 .$$

It is thus necessary for mechanical equilibrium that neither ρ nor p vary in horizontal planes. The same must then hold good of T, which is determined by ρ and p through the equation of state of the liquid. But radial heat flow in the cell (with vertical wire) is incompatible with the isothermal surfaces being horizontal planes.

In [2], pages 17-19, is therefore given what the author considers a more reliable investigation than the usual one of the convection problem. The result will be mentioned briefly in the next section.

Furthermore, a thermoelastic source of error, which may appear in certain designs of the cell - e.g. in the design used by Gillam et al. [13] - and which is not mentioned in the literature, is schematically treated in [2] pages 29-37. It is shown that - although the error would (at least in principle) appear in the author's set-up (in which the hot wire is not stretched by a spring) at absolute measurements - it is completely eliminated by the relative procedure followed. But it may have played a role at certain absolute measurements given in the literature.

The remaining part of [2] contains the more trivial - but necessary - elementary circuit analysis and description of the calculation method for λ which is valid for measurements on pure, dielectric liquids with the author's set-up. In the literature on the method it seems that it is always considered necessary to use as thin a wire as possible (e.g. 20 μm in diameter) in order to approximate a line source distribution for the heat. This makes the main features of the theory very simple (if the line source is also considered infinitely long). But nevertheless corrections are worked out by more recent authors (e.g. in the very careful work [13] by Gillam et al.) to the simple "line source theory". The underlying idea of the present modification, mentioned above, made it necessary to break with the "classical principle of the thinnest possible wire" and to use a "thick" hot wire (500 μm in diameter). The said analysis in [2] therefore differs somewhat from the more usual one and it turns out that it is not necessary to make a detour round the idealized line source, later correcting for this idealization. Using an iterative procedure it is possible to set forth directly a method of calculation for λ from the readings in the set-up during the measurement. Incidentally, the use of a "thick" wire and the omission of the spring used by many researchers for stretching the wire resulted in a very simple and robust cell construction (cf fig. 6, page 21).

The modification of the method to apply to electrolytic solutions is described in [3]. In that report the discussion of the underlying theory is intentionally limited. [3] mainly describes the experiments carried out at the semiautomatic stage (cf page 6). But in [4] the theoretical foundation of the modification is treated more thoroughly.

Let us consider a simple electrolysis system made up of a vessel containing an electrolytic solution and 2 platinum electrodes. If a voltage below the decomposition voltage of the electrolytic solution is applied to the electrodes a current will flow between them although the voltage is below the decomposition voltage. Ions are transported to and from the electrodes owing to the electric field in the liquid. In what has in [3] and [4] been termed 'the non-faradayan case' the ions make up parts of the interfacial layers metal - liquid and finally destroy the electric field in the solution which initially was caused by the charges on the electrodes. The process then ends up with equilibrium after a (short) pulse of current through the solution. In [4] is mentioned that this phenomenon does occur and that it is perhaps more common than one might think. Perhaps one would - at least from a macroscopical point of view - expect that non-faradayan current pulses were merely an "academic" abstraction because the ions arriving at and leaving the interfacial layers may cause displacements of possible chemical reactions in the layers.

Such "faradayan" phenomena of course also occur. As long as the applied voltage is not increased above the decomposition voltage of the solution (+ "overvoltage", if any) there will, however, be no formation of new phases of electroneutral products because the products have not reached their saturation concentrations. The products - formed in very small amounts - will then begin slowly to diffuse out from the interfacial layers into the bulk of the solution. Hence, in the "faradayan" case one will not end up with a thermodynamically stable equilibrium but in practice one may consider the current as almost died out after some time. Hence one may distinguish between two types of current pulses below the decomposition voltage: "faradayan" and "non-faradayan" ones.

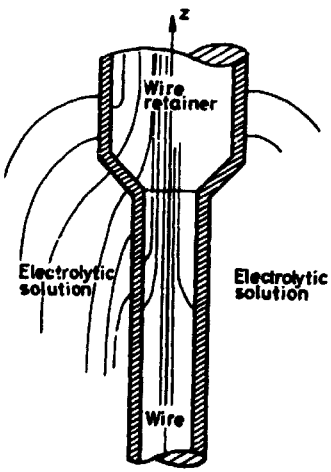


Fig. 1

Now, in the measuring cell one of the wire halves and its retainer corresponds to one of the electrodes in the simple electrolysis system considered above. Ions are thus transported in curved paths through the solution from one wire half ("plus" retainer) to the other wire half ("plus" retainer) as sketched in fig. 1, where the curved lines indicate the instantaneous streamlines of charge "resulting" from the ion transports. At the outset the (curved) interfacial layer between wire and electrolytic solution is homogeneous in the direction of the wire, z. But during the process anions and cations are transported to different wire halves (and retainers) and the layer will accordingly become differently composed along the wire. The composition of the interfacial layer will vary continuously in the z direction during the process. In [3], page 12 it was mentioned that this fact makes it possible that a jump occurs in the z component

of the electric field during passage through the layer from wire to solution. It is therefore possible to end up with no current in the liquid but with current in the wire. According to the "usual" jump condition for the Maxwell equations concerning the tangential component of the electric field - i.e. its continuity - one might expect that this is not possible since according to Ohm's law there must in an homogeneous phase be a current density proportional to the electric field. The author has never seen mentioned in the literature that the said jump condition is not generally valid, but here one evidently has a case in which the very understanding of the process in the system studied is dependent on the invalidity of that condition. This has been discussed in detail in [4], pages 46-47.

It is very important that the current pulse can be made small and quick enough by modifying the set-up because in an unmodified set-up the current in the liquid may disturb the registrations also when one is able to operate below the decomposition voltage δ of the electrolytic solution. Here it may be added that it is self-evident that there must be no electrolysis during the measurement as would be the case if δ(+ overvoltage) is exceeded. E.g. electrolysis of many aqueous solutions gives rise to bubble formation along the wire and the heat flow must of course not meet such bubbles on its passage through the liquid during the measurement.

Now, in order to demonstrate that the current pulses in the solution (when the applied voltage is $< \delta$) may disturb recordings in a "classical", unmodified set-up and that they do not in a set-up modified as described in [3], the "field theoretical" fig. 1 was in [3] replaced by fig. 2 with "lumped" electrical parameters. In fig 2 (on the next page)

- I = the current fed to the cell
- I_W = the current in the wire
- I_L = the current in the liquid column
- R_L = the resistance of the liquid column
- R_W = the resistance of the wire
- $\mathcal{E}_1$ and $\mathcal{E}_2$ = counter electromotive forces

Fig. 2 is of course much more handy than fig. 1 but, strictly speaking, the change to it requires some justification. A fairly detailed justification is made in [4] and it turns out that fig. 2 is not strictly correct but fully adequate for the purpose: Strictly speaking there are some points in the change fig. 1 → fig. 2 that must be discussed. Firstly, the interfacial layers are represented electrically by electromotive forces, and secondly

Fig.2

the current paths in the solution are curved so that it is not evident that the liquid could be represented by a resistance = the resistance in the z direction of the liquid column. Thirdly, no account is taken of induction in the "model" fig. 2 and in the formulae connected with it in [3]. Finally I^* (see the figure) is put equal to I_L. Since this means that the total charge of the interfacial zones round a wire half ("plus" its retainer) vanishes during the pulse it is not exactly correct. But it turns out in [4], pages 56-57, to be an extremely good approximation. The investigation of these points requires some technicalities and, as mentioned, it has been carried through in detail in [4], but there seems to be no reason for repeating the main points of that investigation systematically in the present survey.

But the model fig. 2 alone does not suffice for demonstrating that the modification described in [3] is correct. The use of fig. 2 was therefore combined with results of using a so-called "blank experiment technique" as will be mentioned shortly. Clearly, if it were possible to calculate quite generally the development in time of the current pulses in the measuring cells it would also be possible to study their disturbing effects purely theoretically and to predict the optimal modification of the set-up. Under certain simplifying presumptions the development of non-faradayan current pulses was calculated in [4] and it was found that such pulses fade out sufficiently quickly not to disturb measurements even in an unmodified set-up. But although such pulses, as mentioned above, do occur in practise (especially at very low applied voltages) there is still the possibility that "faradayan" complications may occur in an actual case. Such complications may delay the initially non-faradayan process. But the author had no opportunity of continuing the theoretical investigations beyond the non-faradayan case, i.e. of investigating whether it would be possible to find reasonable limits of "faradayan" delays. Therefore the "blank experiment technique" mentioned still plays an essential role if the author's modification is used and that technique will now be briefly outlined.

If, instead of the platinum hot wire, a manganin wire with the same resistance is inserted in the cell, the change of the wire resistance during the heating will be so small in a period equal to the usual measurement period of λ determinations that it cannot be registered. At such an experiment with the electrolytic solution filled into the cell one would expect disturbances from current pulses to reveal themselves. True, this also holds good, but a few comments must be made.

It is found in [3], page 22 that during such a "blank experiment" the resistance of the cell, R_C can be written on the form

$$R_C = \frac{\text{const.}}{1 + \xi} ,$$

where ξ is a parameter which accounts for how far the balancing of the voltage applied to the cell by the polarization has proceeded. Now, what is registered by the recorder - which is usually used for blank experiments also after the introduction of full automation of the λ measurements themselves - is the change of R_C, and the whole development in time of ξ during a blank experiment may therefore be inferred from the recorded diagram. But the question is then whether it is possible from the course of ξ during a blank experiment to infer the course of ξ in an experiment for determination of λ. For that inference to be possible it is first and foremost a condition that the manganin wire does not catalyze the possible electrode processes positively or negatively as compared to the platinum hot wire. Such a catalysis from the manganin might very well occur. Manganin contains e.g. Cu, and, as is well known, Cu^{++} catalyzes many processes. But the said possibility may easily be precluded: the manganin wire is placed outside the cell as sketched in fig. 3. (The thick Cu-"blocks" are used in order not to introduce "new" resistances). In the cell the electric current will then flow through the solution between the retainers until it fades out. If the retainers are not made of platinum, but e.g. of stainless steel as in the apparatus used, small bits of platinum wire may be inserted in the retainers during blank experiments so that any catalytic effect from Pt in the "main experiments" also occurs in the blank experiments.

That the current in the blank experiments flows between the retainers only and not also from one half of a wire to another half of a wire through the solution as in the λ-measurements does not mean anything as far as the inferences from blank experiments to λ-measurements are concerned. This has been demonstrated experimentally by extending the platinum wire bits mentioned to almost wire halves which only did not touch each other. The

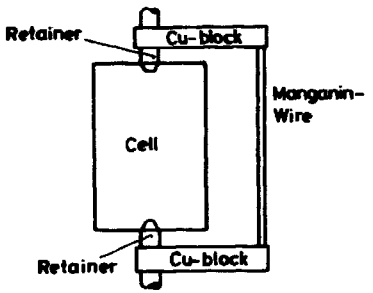


Fig.3

blank curves on the recorder did not change in the least thereby.

At the initial stages of the λ measurements the changes of R_C (the cell resistance) is dominated by the current pulsee - i.e. by changes in ξ - and at the later stages the R_C-changes are due to the rise in temperature T. In [3], page 20, it is shown that during a measurement one has for the registered cell resistance

$$R_C = \frac{R_W}{1+\xi} = \frac{R_W(T)}{1+\xi}, \quad (1)$$

where ξ is now dependent also on T, and R_W = the resistance of the wire, which in its turn is determined by T. Thus it is seen that one cannot treat the registered changes of R_C as the superposition of two independent contributions from ξ changes (determined by blank experiments) and from T changes. Thus one cannot use the blank curves so that one "subtracts" them from the measurement curves in order to obtain "true" measurement curves. But it is shown in [3], section III that what is needed to transfer from blank experiments to measurements in the modified set-up is only the "initial value of ξ", i.e. the value of ξ after the non-faradayan part of the pulse is almost instantaneously over, and that transference can be safely made. The temperature of the wire does not increase to any registrable extent during the non-faradayan part of the pulse.

Figures 4 and 5 show examples of registered "blank curves" in an unmodified, classical set-up (fig. 4) and in a modified one (fig. 5). The figures are tracings of recorder diagrams reduced to half size, and they clearly show the essential difference between the classical and the modified apparatus. (The different scales along the voltage axes should be noted). For comparison one ought, strictly speaking, to have taken curves stemming from the same electrolytic solution. But the figures are reproductions of two figures in [3], page 48. Fig. 4 was chosen at random among blank curves

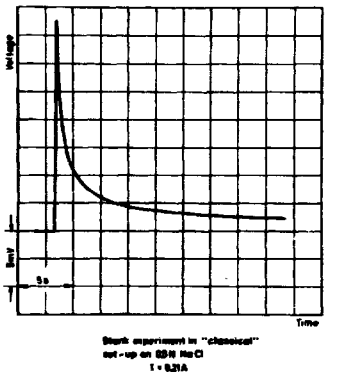


Fig.4

On figures 4 and 5 the registered voltage is positive "downwards".

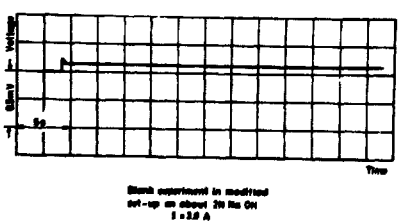


Fig.5

from the classical set-up, and it is characteristic of such curves from the solutions studied in [3]. The same holds good for fig. 5, but electing it, the author thought it would be most relevant to choose a curve stemming from a strong base, since the main purpose of the modification is - as opposed to[a] Alas [1] - to extend the measurement range of the method to comprise also bases.

An example of the usefulness of the blank experiments may be mentioned here: during the work concerning widening of the measurements,

[a] cf page 6.

the author tried to measure on aqueous HCl solutions, making as usual blank experiments before measuring. The blank curves turned out to be completely different from fig. 5 and were not even reproducible. The explanation must be that the stainless steel used for the wire retainers reacts at low p_H-values through p_H-dependent processes with small amounts of Cl_2 produced by the current pulse. At higher p_H values in solutions containing Cl^- there are no problems of this kind, e.g. the blank curves stemming from Na Cl solutions were always equal to fig. 5 and completely reproducible. What has been said here does not mean that the method has some serious shortcomings. If one uses a coating of a suitable material round the wire retainers, the problem concerning measurements on HCl and acid solutions of chlorides is probably eliminated. True, platinum will also be able to react with Cl_2 but presumably only to such a small extent that it does not disturb the measurement. As a matter of fact a film on the stainless-steel wire retainer, presumably produced by reaction with Cl_2, could be directly seen after repeated switchings on and off of the current. But the author had for practical reasons no time to extend the range of applicability of the apparatus to comprise also such exceptional cases as acid solutions containing Cl^-. That is the reason why the list of solutions measured on in the present work does not comprise HCl solutions among the acid ones.

The "blank curve" fig. 4 registered with the classical set-up and stemming from so "ordinary" a liquid as 0.5 N Na Cl does not correspond to a non-faradayan current pulse. This has been demonstrated in [4], page 64. Hence "faradayan complications" must generally be expected when measuring on electrolytic solutions. As indicated the initial stages of a current pulse must always be non-faradayan: the ions must be transported to the interfacial layers between electrodes and solution before chemical reactions can occur in these layers. It is therefore important, in spite of the possibility of faradayan delays, to study non-faradayan pulses: their development in time is, also in the faradayan case, one of the factors determining what was on page 14 called 'the initial value of ξ' in the formula for R_C. Before concluding this section the investigation of non-faradayan pulses in [4] will therefore be briefly indicated.

In section III of [4] the investigation of non-faradayan pulses is carried out by first stndying a "simple electrolysis system" made up of a glass tube and 2 platinum discs forming the top and the bottom of the tube and serving as electrodes. The, as it appears, non-linear differential equation for the development in time of a non-faradayan pulse through an electrolytic solution between the electrodes is derived. By following a similar, but more complicated, way of reasoning, the equation for the actual measuring cell

with the wire inserted is derived in section IV of [4], and the modification of the classical set-up to comprise also electrolytic solutions is justified on the basis of that equation and the further reasoning in the said section of [4].

At the outset of the work, it was found that the equation for the "simple electrolysis system" could not be found in the literature - at least not in a form which was directly applicable to the present case -. In other words it appeared that the problem is not quite as elementary as it seemed to be. Intuitively one might consider the charges in the platinum discs and the charges of the ions transported to them as constituting double layers corresponding to simple condensers at each electrode. These condensers would then be in series, connected by the resistance of the liquid column. Such a model of the layers has been set forth many years ago (by Helmholtz), but the model has turned out to be inadequate for quantitative reasoning. The reason is not only that the distance between the charges in such an "electrode condenser" must be known for calculations to be carried through. One may estimate the said distance to be of "atomic" order of magnitude and use the model as a first approximation. This is done in the small print text pages 28-31 of [4] for the purpose of comparison with more reliable calculations because it seems that this simple "Helmholtz-model" is - in any case among non-specialists - still considered applicable to a certain extent.

For qualitative reasoning one clearly need only a model that - as does the Helmholtz-model - explains a "jump" in electric potential through the interfacial layers between solution and metal, but for quantitative reasoning "the mechanism" producing the "jump" is important. In what may be termed 'a pure condenser' the charges form single layers, separated by a dielectric layer or a vacuum. Thus in the Helmholtz-model the potential "jump" is governed by the electrodynamics of dielectrics. Gouy, however, was the first to note that, owing to thermal motion, the particles cannot be supposed to be distributed in single layers but must form more extended diffuse layers. According to the Gouy-model, the layer at an electrode can therefore be considered composed of two diffuse layers, one in the metal and one in the solution, the two layers being separated by a mathematical surface. In this model dielectric polarisation is ignored and the potential "jump" is explained by the electrodynamics of electrically conductive phases. This provides quite another foundation for calculating the "potential jumps"; now Ohm's law is applicable to the layers, and in its general form that law contains terms owing to electromotive forces in regions where there are concentration gradients of ions. In equilibrium states the "potential

jumps" are balanced by such electromotive forces (i.e. counter electromotive forces) calculable from the laws of thermodynamics. In the model of the measuring cell with lumped parameters, fig. 2, the layers between wire and solution must therefore, according to the Gouy-model, be represented by electromotive forces. Strictly speaking these electromotive forces must be in series with ohmic resistances, but owing to the extremely small thickness of the layers these resistances may be ignored. Furthermore - as pointed out in [4], page 29, - the distribution of charges in the metal part of the interfacial layers may be considered degenerating into surface distributions *).

The model sketched here, i.e. the "Gouy-model", which is from 1910, constitutes the foundation of the author's calculation of the passing off of non-faradayan pulses in [4]. Regarded as a modern foundation of this calculation the model may seem somewhat primitive and of course it is - to a certain degree -, but in [4] was mentioned i.a. a work by Macdonald and Barlow [16] from 1962 indicating that the Gouy-model is still considered able to provide correct quantitative results in cases of low ionic concentrations and small potential jumps. Owing to lack of time the author had, before publishing [4], been prevented from studying the literature on electrode kinetics of the very latest years. But after having now studied such modern treatises, as e.g. Bikerman [5] (1970) and Erdey-Grüz [10] (1972) he still feels convinced that the Gouy-model constitutes an adequate foundation for the present purpose, i.e. to explain theoretically the success of the modification. Thus Bikerman, loc.cit. page 371, writes that the Gouy-model of the liquid part of the interfacial layer is still "generally" considered correct in the limit for small potentials and concentrations.

It seems as if the Gouy-model and later, more refined models, where "specific absorption" of ions and the influence of dielectric components are taken into account, are still mainly used in the literature for calculations concerning equilibrium. It may therefore be a little objectionable that the Gouy-model has in [4] been used for the calculation of the development in time of the current pulses, not so much because the model is inadequate for the treatment of transient problems, but because some simplifying presumptions were made in connection with its use in order to profit by its simplicity. Thus freedom of mechanical convection in the Gouy layer was presumed, and this presumption was, in its turn, based on the permissibility of ignoring temperature changes during the (very short) time

*) Cf also the footnote on page 36 of [4].

of the passing off of the pulse. Having seen the work [10], the present author now realizes that convection in the Gouy layer is also caused by differences in mass density owing to changes in concentrations during the ion transports to and from the layers. But as mentioned, the Gouy-model is only considered correct at low ionic concentrations in the layers and its use has therefore in [4] been combined with the laws of diluted solutions. In diluted systems there is, however, no possibility of changing the mass density field ρ strongly. In other words, it is reasonable to consider ρ fairly constant as long as no appreciable temperature increase is involved i.e. to neglect convection. Studying more concentrated solutions one has to use more refined models of the interfacial layers between metal and solution.

If the whole study of the disturbing pulses in [4] should be carried out, not only for the purpose of giving reasonable lines of direction for the modification and an explanation of the success of that modification, but also for the purposes of exact predictions, it should presumably be brought in accordance with works similar to those of K. Miller [19] and Hashimo [15]. In [19] a detailed study is given concerning layers between metal and electrolytic solutions, the metal part being platinum, and in [15] is given a treatment of the problem in which use is made of statistical thermodynamics and solid state physics.

Now, as it is seen from the above, the problem of the structure of the interfacial layers and the processes in them is not quite elementary. It would therefore be convenient if one could confine the investigation to the bulk of the solution. The bulk of the solution can be considered chemically homogeneous during the passing off of the pulses, and if rises in temperature are ignored it is derived in any textbook on electrodynamics that the current density must fulfil a vector wave equation. But it seems impossible to give correct initial and boundary conditions for that equation. A model of the surface layers and the taking account of the remainder of the circuit through a circuit analysis must replace the needed knowledge of the said conditions. Only if one makes an ad hoc assumption - namely that the term owing to induction in Ohm's law on <u>differential</u> form can be neglected even during the study of such a fast process as the fading out of the pulses - is it easy to find a solution without difficulties originating in the interfacial layers. But the result is erroneous, as pointed out in [4], pages 19-20. The reason why it has been mentioned at all in the said work and in the appendix of [3] is that to a certain degree the result seems to be supported by reasoning found in a very well-known and estimated book on electrolytic solutions (cf [4], page 20).

Studying the "simple electrolysis system" mentioned on page 16 and using the Gouy-model the differential equation for the passing off of the

non-faradayan pulses is, as mentioned above, derived in [4], section III. The considerations are confined to a strong "1-1" electrolyte. The result is that if 'q' denotes the average charge per unit area of the liquid Gouy layer of one of the electrode plates, and if external resistance in the leads from the source is ignored, one has

$$\frac{\dot{q}}{\sqrt{(q^2+n)}} + m\bar{q} = 0 \quad . \tag{2}$$

Here m and n are known constants given in [4], pages 40 and 37, and dots denote differentiation with respect to time. This equation - although not linear, as it would be if an elementary condenser model were applicable to the layers - is easily solved. The general solution is given in [4], page 41 but the expression is not handy. (2) is therefore in [4] combined with certain experimental facts given by Forker [12] (and other authors), and it is derived that the current I_L in the liquid will under non-faradayan conditions fade out more quickly than corresponding to an exponential decrease

$$I_L = I_0 e^{-\frac{t}{\tau_2}} \quad , \tag{3}$$

where I_0 = the initial value of I_L and τ_2 is a time constant which is calculated in [4], page 43. 't' denotes time. During this derivation, induction is ignored in the circuit analysis with which (2) is also combined. But induction is only ignored, when Ohm's law is used on integrated form, not on differential form. The integrals of the "induction terms" (over distances and cross sections in the system) may very well be approximately negligible, although the terms themselves in the differential expressions are not negligible. This is pointed out in [4], page 26, and a support for neglecting induction in the integrated equations in the present work is given in [4], page 27. For a system with dimensions like those of the actual cell used in the author's experiments, and filled with a 1N KCl solution, it is found that

$$\tau_2 \simeq 4 \cdot 10^{-3} \text{ second} .$$

After this (2) is altered in [4], section IV so as to be applicable to the actual system with a wire inserted along the axis of the cell. It turns out that the altered form - 'q' now denoting the average charge per unit area of the liquid Gouy layer around one wire half and its retainer - is

$$\frac{\dot{q}}{\sqrt{(q^2+n)}} + \alpha \frac{A_W}{4 A_C} m\bar{q} = 0 \quad ,$$

where A_W = the area of the surface of the wire and its retainers, and A_C = the cross section of the cell. α is a quantity which, through rather lengthy considerations, is seen in [4], pages 48-53, to be approximately equal to unity. Hence, with approximation

$$\frac{\dot{q}}{\sqrt{(q^2+n)}} + \frac{A_W}{4 A_C} \cdot m\bar{q} = 0 \quad , \tag{4}$$

where the "form factor" $\frac{A_W}{A_C}$ is < 1. The form factor clearly alters the

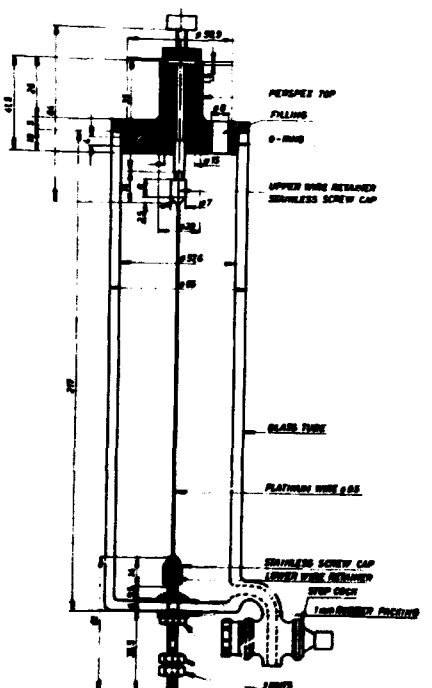


Fig 6

previous value given for τ_2, and it does so in a favourable way. A glance at fig. 6, which is a sketch[a] of the modified cell shows, however, that A_W is - even in the modified cell with its "thick" wire (cf page 9) - mainly determined by the contribution from the wire retainers. The retainers have for reasons mentioned in [2], page 26, been given rather large cross sections. Thus there will be no significant difference between the altered τ_2 values for the classical and for the modified cell if A_C and the shape of the retainers are the same for the two cells. This fact is also interesting with regard to the blank experiments, during which the wire is removed and the current in the liquid flows only between the wire retainers; also in blank experiments τ_2 will have almost the same value as in "main experiments" (i.e. λ measurements) in the classical and in the modified set-up. This was not clearly pointed out in [4].

According to the above one would expect that (4) is also applicable to the "simple electrolysis system" to which (2) applies, namely if the contribution to A_W from the wire is put exactly = 0 and the retainers are imagined replaced by plates forming the top and the bottom of the cell. Since there are 2 plates it might be expected that one had to put $A_W = 2 A_C$ in (4) in order to obtain (2), but (2) is only obtained by putting $A_W = 4 A_C$. This is due to the fact that (4) has been derived under the presumption that the curved surfaces of wire and retainers are vertical almost everywhere[aa]. Therefore (4) cannot be used for a "simple system" in which the plates are horizontal. Accidentally (4) is correct in the case where the (horizontal) plates are not extended to the cell wall and do not form the bottom and top of the liquid column i.e. are completely surrounded by the liquid. Since each plate has 2 sides one had in that case to put $A_W = 4 A_C$ if the validity of (4) were not limited by the mentioned presumption.

In the above we had in mind a somewhat simplified model of the apparatus. Resistances outside the cell were ignored and it was not taken into account that the circuit is ramified, the cell being a component of a wheatstone bridge in the actual set-up. That set-up is shown on fig. 7, and on fig. 8 "Bridge I" is a characteristic example of a bridge in a classical set-up, "Bridge II" is the modified bridge. In both cases E = 12 volt, but the external resistance R, the resistances of the bridge, and the current I fed to the bridge are very different. In the classical case (bridge I) R was $\simeq$ 50 Ω and I $\simeq$ 0,2 A. (Here it should be mentioned that in the author's previous work with a classical set-up the resistance of the wire was not 10 Ω as indicated on fig. 8 but 16 Ω for reasons given in a footnote in [2], page 43. Fig. 8 was originally used for some rough estimations concerning the possibility of modifying the method at the outset of the work). In the modified set-up R was $\simeq$ 3 Ω and I $\simeq$ 3,5 A.

[a] All dimensions are given in mm.

[aa] Cf fig. 6.

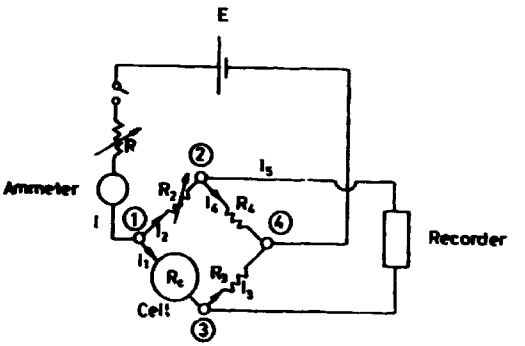


Fig.7

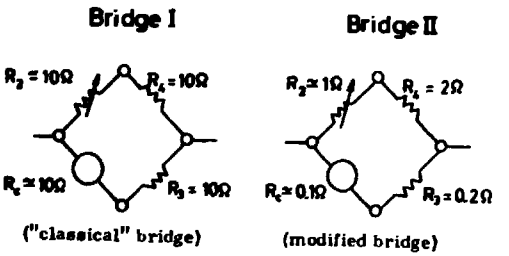


Fig.8

Now, taking the ramification into account, it is found in [4], page 60, that

for the classical set-up: $\tau_2 \simeq 8 \cdot 10^{-4}$ second ,

and for the modified set-up: $\tau_2 \simeq 3 \cdot 10^{-4}$ second.

In order to compare the classical and the modified set-up with regard to non-faradayan pulses one must according to (3) - which is valid also in the ramified system - furthermore compare the initial values I_0 of the current I_L in the liquid. In [4], pages 60-62, the necessary calculations are carried out and finally it is found that for non-faradayan pulses one has under the presumptions made in [4] (small applied voltage, applicability of the laws of diluted solutions in the interfacial layers, the electrolyte being a strong "1-1" electrolyte):

for the classical set-up: $I_L \simeq 0,1\ e^{-1.3 \cdot 10^3 t}$ A ,

and for the modified set-up: $I_L \simeq 0,07\ e^{-3.3 \cdot 10^3 t}$ A .

where t = the time after switching on the current measured in second, and I_L is the current in the liquid corresponding to the "limiting" case (3), i.e. to the slowest development in cells of dimensions as those used in the present work and circuits as described above. It is seen that τ_2 has been improved $\frac{3,3}{1,3}$ times and I_0 $\frac{10}{7}$ times by the modification.

These improvements do not seem to be very *significant* but, as a matter of fact, it is seen in section IV of [4] that they need not be so: If all pulses through the liquid were non-faradayan, (i.e. non-faradayan in accordance with the presumptions just mentioned) no modification was necessary at all. The pulses would then have died out sufficiently quickly not to disturb registrations also in the unmodified set-up. The kernel of the modification therefore concerns the faradayan case.

In [4], page 10, is given a quotation by Delahay [8] showing that - as mentioned above - non-faradayan pulses are not only "academic" abstractions. They really do occur, but no general rules exist according to which it can be predicted if an actual case is "non-faradayan" or "faradayan", and on page 16 an example of the latter was given. Hence one must generally reckon with such complications. But - as indicated above - it is clear that at the initial stages the current pulses must always be non-faradayan. It is therefore essential that the modification has improved the development of non-faradayan pulses - or, maybe, rather that it has not worsened it - at the same time as it has improved quite essentially the possibility of supressing faradayan complications, as will be mentioned now.

In formula (1), page 14 the quantity ξ, which accounts for the pulses can, according to [3], page 16, be written on the form

$$\xi = \frac{R_W}{R_L} p ,$$

where $0 \leq p \leq 1$, and R_W and R_L are the resistances of the wire and the liquid column respectively. This is valid independently of the pulses being faradayan or not. Hence, according to (1) one has for the cell resistance R_C

$$R_C = \frac{R_W}{1 + \frac{R_W}{R_L} p} . \tag{5}$$

At the moment, t = 0, the current to the cell is switched on, p = 1. At $t = \infty$, p = 0. Hence R_C may, during a λ measurement, run nearly through the interval

$$R_W - \frac{R_W^0}{1 + \frac{R_W^0}{R_L^0}} = \Delta\tilde{R}_C , \tag{6}$$

where index '0' indicates initial values. If the liquid were dielectric, one would constantly have $\xi = 0$, i.e.

$$\left.\begin{aligned} R_C &= R_W , \\ R_W - R_W^0 &= \Delta\tilde{R}_C \end{aligned}\right\} \tag{6a}$$

and it is seen from (6) and (6a) that it must be an improvement to make

$$f = \frac{R_W^0}{R_L^0}$$

small. Such an improvement has certainly been obtained through the modification: In [3], page 21, is found e.g. for a 1 N aqueous solution of K Cl at 25°C that for cells of the dimensions used, one has

for the classical cell (wire radius = $1,5 \cdot 10^{-3}$ cm)	and for the modified set-up (wire radius = $0,25 \cdot 10^{-1}$ cm)
$f = 4$,	$f = 1,4 \cdot 10^{-2}$.

But this improvement is not enough. A necessary condition for making the method work is that the deviation of the (indirectly) registered R_C from R_W will be so small that it can be neglected fast enough, i.e. before R_W is changed registrably owing to heating. If R_C changes simultaneously owing to the pulse and owing to the heating the changes interfere and cannot be separated. According to (5) they can not even - as mentioned before - be superposed so that one cannot "subtract" the diagrams of blank experiments from diagrams of λ measurements in order to obtain "true" diagrams.

Now, the total change of R_W owing to heating during a measurement of λ, ΔR_W, is, according to [3], page 21, about $7.4 \cdot 10^{-2}$ Ω for the classical and about $1.2 \cdot 10^{-3}$ Ω for the modified set-up. $\Delta\tilde{R}_C$ is, according to [4], page 64, about 12 Ω for the first-mentioned and about $2 \cdot 10^{-3}$ Ω for the last-mentioned apparatus during blank experiments. Hence, '$\Delta\tilde{R}_C$' referring to such ones

for the classical set-up: $\frac{\Delta R_C}{\Delta R_W} \simeq 160$,

and for the modified set-up: $\frac{\Delta\tilde{R}_C}{\Delta R_W} \simeq 1.7$

True, $\Delta\tilde{R}_C$ and ΔR_W are of the same order of magnitude in the modified set-up, but as mentioned before all current pulses must commence as non-faradayan ones, and these are - in the present context - extremely fast. In [4], page 63, it is e.g. shown that

$$\frac{R_W - R_C}{R_W} = 10^{-4}$$

at $t = 7.1 \cdot 10^{-3}$ second in the classical and at $1.6 \cdot 10^{-3}$ second in the modified set-up in the non-faradayan case. The cell resistance R_C therefore runs through a high fraction of $\Delta\tilde{R}_C$ nearly instantaneously before faradayan delays may be registered. According to the above there is (cf [4], page 65) a high probability of having blank curves as fig. 5 in the modified and as fig. 4 in the classical set-up. Fig. 5 is characteristic of all the blank curves corresponding to the measurements on 14 electrolytes, each in various concentrations, mentioned in the experimental part of the present work, and according to the analysis in [3], section III, this means that the current pulses through the liquid did not disturb the measurements.

Since for practical reasons the author has had no possibility of studying theoretically faradayan complications in detail, the blank experiments must still be considered a necessary part of the modification if one wants to be on the safe side, but they are easy to perform, so that this fact can hardly be considered a drawback.

Finally it should be noted that the scales on the voltage axes of fig. 4 and fig. 5 are different. Using the classical set-up (fig. 4) it was necessary to diminish the sensitivity of the recorder 10 times in order to keep the curve on the paper. Although one cannot subtract the blank curves from the measurement curves in order to obtain "true curves" this can be done to a rough approximation - especially for the modified apparatus - and it is seen that in the classical one the true curves are - quite apart from their being approximations - too "small" to be usable.

II. On the General Macrophysical Foundation of Measurement of the Thermal Conductivity of Fluid Materials

In the literature on measurements of the thermal conductivity of liquids, the "heat flow equation" without "source terms" usually forms the basis, assumed beforehand, of the treatment. Without source terms the "heat flow equation" reads

$$\lambda \nabla^2 T - \rho\, c_p \frac{\partial T}{\partial t} = 0 \ ,$$

where

λ = thermal conductivity
'∇^2' refers to space coordinates
t = time
T = temperature
ρ = mass density
c_p = specific heat at constant pressure

This equation has in principle some shortcomings. If e.g. λ, ρ and c_p can be considered constant in time and space*) throughout an infinite, homogeneous medium - as is permissible in cases of only small temperature differences in the medium - the equation has the following property. If a point source is introduced at $t = 0$ in the medium there will according to the equation be an (infinitesimal) temperature rise infinitely far from the source after the lapse of an infinitely small time, after the introduction of the source. Thus the heat has been transported with infinite velocity through the medium. Although one does not, of course, need a relativistic foundation this may

*) This is usually assumed when the said equation is used.

be taken as an indication of the equation being only an approximation. One might rather expect the temperature disturbance to propagate with the velocity of sound of the medium cf [20], page 135 and [18], page 865.

Let us consider a pure, dielectric liquid. In [2], pages 9-13, it was shown that, in cases where thermal radiation can be neglected, the general balance principles and the constitutive equations of microscopical physics lead to the following equation (which is a well-known result, not a result discovered by the present author):

$$\rho\, c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = -\rho\, c_p \vec{v} \cdot \operatorname{grad} T + \operatorname{grad} T \cdot \operatorname{grad} \lambda + \alpha T \frac{dp}{dt} + \Phi$$

where

$\vec{v}$ = the velocity field in the liquid

α = the volume expansivity of the liquid

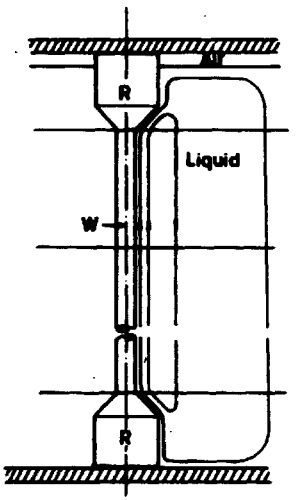
$\frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v} \cdot \operatorname{grad}$ (= convective derivative)

'Φ' is a term owing to internal friction.

As there are no general physical principles according to which it can be proved that the right-hand side of this equation is equal to 0, it follows that the simple "heat flow equation" is not strictly correct. As mentioned in [2], page 20, we may, for our purpose, neglect the three last terms on the right-hand side of the correct equation, and we have for a pure, dielectric liquid:

$$\rho\, c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = -\rho\, c_p \vec{v} \cdot \operatorname{grad} T.$$

Now, in the previous section it was mentioned that all authors treating the hot-wire method postulate or try to prove - at least to the present author's knowledge - that $\vec{v} = \vec{0}$ during the measurement period. If this were so, the simple heat flow equation would apply immediately. But using small particles of earthmoss-seeds, distributed in the liquid, the present author found, as mentioned in the previous section, that lively convection sets in long before the measurement period, traditionally used, has elapsed. When that period is exceeded the convection even becomes rather wildly turbulent, but it seems as if one may generally state that within the measurement period it is laminar and that $\vec{v}$ is directed vertically in a region corresponding to



(R = retainer, W = wire)

Fig. 9

the vertical hot-wire. At the ends of the cell, on levels with the wire retainers this does of course not hold good. Fig. 9 shows schematically the instantaneous streamlines during the laminar period. By making the wire retainers rather large it was avoided that they participate in the heat production so that in the author's set-up it is almost only the said region which is important.

Now, although $\vec{v} \neq \vec{0}$, the term '$\rho\, c_p \vec{v} \cdot \operatorname{grad} T$' would also be negligible if it could be seen that $\vec{v}$ and grad T are almost perpendicular to each other in the important region. This cannot be exactly true, because it was observed that the upward flow along the wire does not reach very far out in the liquid during the measurement period. That flow was as a matter of fact rather distinctly delimited by a vertical cylindric surface close to the wire, and one would expect the temperature of the liquid to increase upwards in vertical direction near the wire (as if it were flowing in an annular tube heated from the inside and insulated outside). But in [2], pages 17-19, it was demonstrated that one can with good approximation consider this effect negligible.

The present author therefore thinks that the explanation of the fact that convection does not make hot-wire determination of λ of liquids - even with relatively long measurement periods - impossible, is not that $\vec{v} \simeq \vec{0}$ but that grad T and $\vec{v}$ are almost perpendicular to each other in the relevant region. What other authors mean when speaking e.g. of the "convectionfree measurement period" (cf quotations [2], page 14) is, in the opinion of the present author, rather: the time within which the convection does not become turbulent.

The above considerations have been confined to pure, dielectric liquids. Proceeding to studying fluid mixtures, the theoretical foundation becomes more complicated. Let us consider the simplest case: a dielectric, binary mixture as compared to a pure substance. The latter obeys "Fourier's law"

$$\vec{q} = -\lambda \text{ grad } T \ ,$$

where $\vec{q}$ = the non-mechanical energy diffusion flow density. That equation is one of the fundamental, constitutive equations making up the foundation of the above, and it defines λ unambiguously. But owing to "cross-effects" between diffusion of chemical components and energy one must for the binary dielectric mixture generally use a constitutive equation of the form

$$\vec{q} = \alpha \text{ grad } T + \beta \text{ grad} \mu \ ,$$

where μ is the chemical potential of one of the components, and α and β are "phenomenological" coefficients of the same kind as λ (i.e. independent of grad T and grad μ). A constitutive equation similar to the above is valid for the mass diffusion flow density $\vec{j}$ of the said component:

$$\vec{j} = \gamma \text{ grad } T + \delta \text{grad } \mu \ ,$$

where 'γ' and 'δ' also designate phenomenological coefficients . From this is seen, if $\varkappa$ and $\varkappa$ are new phenomenological coefficients, that

$$\vec{q} = \varkappa \text{ grad } T + \varkappa \vec{j} \ ,$$

which is different from the simple Fourier-law

$$\vec{q} = -\lambda \text{ grad } T \ ,$$

valid for a pure substance. In [4] , section V, it is mentioned that this means that it is not clear what is meant when speaking about "the thermal conductivity" of a binary, dielectric mixture: If, e.g., $\vec{j} = \vec{0}$ another result is obtained than if $\vec{j}$ is $\neq \vec{0}$ and determined by grad T, as will be the case if the mixture is chemically homogeneous (and there are no pressure gradients). In that case μ depends on T only. In the first case one has

$$\vec{q} = -\lambda_1 \text{ grad } T \ .$$

In the latter case one has

$$\vec{q} = -\lambda_2 \text{ grad } T \ ,$$

and $\lambda_1 \neq \lambda_2$. Hence the concept of thermal conductivity of liquid mixtures is ambiguous. This is not a discovery made by the present author but is stressed in every textbook on non-equilibrium thermodynamics, see e.g. Haase, [14] page 365.

In the said section of [4] was investigated a little closer if this ambiguity of the concept of thermal conductivity is only of "academic" interest - the differences between λ_1 and λ_2 being always negligible - or if there may be cases in which it plays a role. It turns out that for binary, gaseous mixtures there may be a significant ambiguity. The different λ values may differ by, say, 2% according to the method which has been used for their determination.

Let us compare a steady state apparatus of the "horizontal-lamella" type mentioned in [2] , page 62, and indicated by fig. 14a of that work with a transient hot wire device.

The steady-state-lamella method has been widely used, especially in former times - and it is still in use. In a set-up for measurements according to that method the liquid fills a "gap" between 2 horizontal planes, which are kept at different temperatures. If we imagine that the apparatus functions ideally, i.e. that the planes are infinitely extended and that the temperature is absolutely uniformly distributed over each of them, it is seen from the reasoning on page 8 that, if the liquid is pure, mechanical equilibrium can be established in spite of the temperature differences in the system. The isothermal surfaces in the gap are then horizontal planes. Furthermore it can be proved that, if the lamella is heated from above, the mechanical equilibrium is stable. In the case of a liquid mixture as the one considered the corresponding investigation is more complicated, the mole fraction of one of the components now being a new independent variable. We shall not delve into that question but simply assume that the result also holds good for the mixture. Doing this, we are in accordance with remarks set forth in de Groot and Mazur [7] , page 44. Now, from the symmetry of the device it is evident that, if $\vec{j} \neq \vec{0}$, it must be vertically directed, which means that $\vec{j} = \vec{0}$ in the final steady state, where div $\vec{j} = 0$. Hence, what is measured, using the steady-state-horizontal-lamella method, is the λ value called 'λ_1' above.

Let us now imagine an ideal transient hot-wire measurement carried out on the same mixture. That it is ideal should be taken to mean that it is made so quickly (with modern electronic equipment) that one may totally neglect convection during the measurement without further discussion.

(Strictly speaking the discussion of the convection problem referred to above is confined to pure liquids). Since $\mu = \mu(T, p, x_1)$, where x_1 is the mole fraction of one of the 2 components and we may neglect the dependence of μ on p for the liquid in the cell: $\mu = \mu(T)$. This is due to the liquid being homogeneous in the initial state and the measurement being made so fast that the effect of thermodiffusion may be ignored. The mole fraction can only be changed by diffusion because we assume that the mixture is chemically non-reacting and hence the mixture remains almost homogeneous, i.e. $\vec{\text{grad}}\, x_1 = 0$. Therefore grad μ is proportional to grad T, and what is measured is the λ value called 'λ_2' in the above. Hence for a binary gaseous mixture the measured λ value may be about 2% different if it is measured by the two methods mentioned. The value of the difference was found in [4] by reference to calculations made in Meixner and Reik [17], page 454. If the accuracy of λ measurements obtainable today is taken into consideration, such a difference is not negligible. At very exact calculations concerning gaseous mixtures a problem therefore arises as to what method has been used if the λ value is taken from a table, in which the method is not specified. But for liquid mixtures it turns out in [4], section V, that the problem probably does not exist - maybe apart from certain exceptional cases -.

III. The Experimental Part of the Work. Measured Values

a) General Remarks

The experimental work proper was excellently done by P. Mørk Christensen who also contributed original suggestions for improvements of the apparatus and organized the computer processing.

The measuring cell is shown in fig. 6, page 21, where all dimensions are given in mm, and the figure gives most of the necessary information about this part of the apparatus. The radius of the wire was measured to be $0{,}500 \pm 0{,}001$ mm, but this value is of minor importance as, within certain limits, a systematic error in it does not play any part on account of the iterative method followed by the calculation of λ, which will be mentioned later. The initial state of the liquid in the cell must be temperature homogeneous. At the beginning of the experiments the temperature uniformity

was checked on 3 resistance thermometers placed at different levels immediately outside the cell which, in its turn, was placed in a thermostat. With the resistance thermometers temperatures could be determined with an accuracy of $\pm$ 0.02°C. Between the individual experiments the cell was at rest for a suitable time. For reasons of convenience a water thermostat with redistilled water was used, and the electrical conductivity of the water was checked from time to time. Besides, the cell was only submerged in the thermostat water as far as nearly to the upper end of the perspex "top" shown in fig. 6. Thus the current was supplied outside the thermostat water through a wire soldered on the upper round nut. The cell was placed in the thermostat on a three-legged, stainless-steel disc, the legs of which were adjustable so that the wire could be placed vertically, sighting in 2 directions perpendicular to each other after a plumb line. The circuit in which the cell was built in is shown schematically on page 23, fig. 7 and fig. 8, Bridge II with greatly rounded values for the resistances. Currents of 3.5 - 3.8 A and measuring periods of 8-10 second were found to give the best results.

As previously mentioned the first version of the apparatus was based on a semiautomatic procedure, the recorder diagrams being measured out manually. At that stage of the experiments the electric source was - as indicated by 'E' on fig. 7, page 23 - an accumulator battery. A single ordinary accumulater was not sufficient because the basic circuit analysis given in [2], pages 38-47 presumes that the variation of the terminal voltage during the measurement period is extremely small. Further the battery should not be greatly discharged after a reasonably comprehensive series of measurements. Consequently five 12 volt accumulators were used in parallel, which gave a considerable battery capacity, but even this was not enough to satisfy the demand on the constancy of the terminal voltage mentioned in [2], page 44.

The ammeter, fig. 7, which was of class 0.1, generally clearly showed a drop in current during the experiments which could not be explained by the resistance change of the cell.

Upon the advice of Arne Jensen an extra circuit - not shown in fig. 7 - was built in through which the battery could for some time before the beginning of the experiments be discharged at the same current as the one that was used at the subsequent measurements. By a direct switch from such a discharge to measurement the desired result was obtained, which Arne Jensen indicated by means of oscillographic recordings. Later L. Palgaard of the Electronics Department, Risø, confirmed by means of very accurate measuring equipment that by using such a preparatory discharge in a suitable way it is actually possible to fulfil the condition mentioned

in [2] , page 44, namely that the terminal voltage changes by less than 10^{-2}% during an experiment. (Palgaard has written an internal note about his measurements).

The components of the bridge were assembled with extremely thick copper rods and copper wires, and it was carefully analysed for contact resistances or components that might be heated appreciably during the experiments and thus falsify the recorder registrations. For this purpose were used what might be termed "blank experiments on pure water": The cell, adopted to blank experiments as shown on fig. 3, page 14, was filled with redistilled water. In such a set-up there will be no registrations stemming from the temperature rise in the wire - and of course no registrations owing to current pulses. The only possible recordings must be caused by temperature rises in other components of the circuit than the cell. After a number of alterations of the original set-up the result was that the recorder diagrams at such blank experiments were straight lines absolutely parallel to the time axis (or rather with the line that the recorder drew "without signal" if the paper was slightly askew).

As mentioned, the values of R_3 and R_4 in fig. 8 are greatly rounded. The 2 resistances were manganin helices fastened to very thick and short copper rods to which also the other bridge components were connected. With a Müller bridge they were measured quite accurately to be

$$R_4 = 2.8125\,\Omega \;;\quad R_3 = 0.2239\,\Omega \text{ at } 20.00^{\circ}C\ ,$$

and their temperature was kept constant by immersion in redistilled H_2O. As the copper rods were practically without resistance, there was no problem of supply resistances to R_3 and R_4. The same applied to the variable resistance, R_2, which consisted of a precision resistance box on which the resistance could be read with 2 decimals. It had its terminals directly connected to the copper rods, and through quite short and thick copper wires it was shunted with a similar box for fine adjustment at the balance adjustment to be mentioned on page 38. From formula (14b), page 40 it follows that $\partial\lambda/\partial R_2$ is small enough to ensure that the reading of R_2 with 2 decimals suffices (also for the full automatic device where the standard error of λ is $\approx 0.5\%$). The standard error of λ was calculated directly on the computer on the basis of 10 determinations. It was generally about 1.5% (often better), i.e. the mean of 10 determinations could be given with the accuracy of $\pm$ 0.5% or less.

Before mentioning the introduction of full automation the method of calculation of λ shall be briefly mentioned. As said in [2] , pages 27-29, the solution of the heat flow equation for an infinite medium with an infinitely long rectilinear line source leads to the following expression for λ:

$$\lambda = \frac{q}{4\pi \frac{\Delta T}{\Delta \ln t}} \tag{7}$$

where

q = the power per unit length of the source.

$\frac{\Delta T}{\Delta \ln t}$ = the slope of the straight line which is the graph in a temperature versus time diagram, the time scale being logarithmic, and the temperature referring to an arbitrary point of the medium.

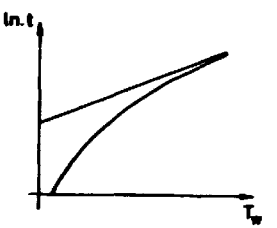
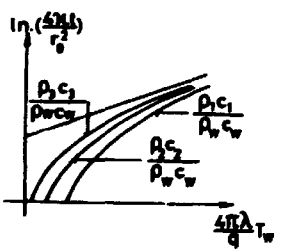


Fig.10



Indices 1,2 and 3 refer to different substances.

Fig.11

To use this expression as the basis of the calculation would be an impermissible oversimplification, among other things because in the apparatus modified by the author the wire is far from being approximately an infinetely long line source. On pages 20-24 of [2] is therefore described a better foundation for the calculation of λ in the present case, namely the equation (17) of that work. That equation, which is given by Carslaw and Jaeger [6] , page 344, is a rather complicated expression which we need not give here. What matters is the following: As indicated it follows from the derivation of (7) that the point at which the temperature T is taken is irrelevant for the validity of that expression. Therefore Eucken and Englert [11] who refined the method [4] in 1938 - after it had been intro-

[4] i.e. the method used for measuring on dielectric liquids

duced by Stålhane and Pyk [26] in 1931 - concluded that one might as well use the wire temperature T_W for T in (7) as for any other point of the medium - neglecting that the wire has a certain diameter and that it is made of another material than the surrounding medium (i.e. the liquid). If this were exactly true one would have a ln t versus T_W diagram as shown by the straight line in fig. 10. But if one uses the more exact solution, namely equation (17) of [2], one finds a curved line, also shown on fig. 10. The asymptote of this curved line when

$$\frac{\varkappa t}{r_o^2} \to \infty$$

is, as showed in Carslaw and Jaeger [6], page 345, the mentioned straight line. Here '$\varkappa$' means λ divided by the product of the mass density ρ and the heat capacity c of the liquid, and 'r_o' the radius of the wire cross section. If dimensionless coordinates are used as in fig. 11 the expression (17) of [2] may be represented by a fixed family of curves, each corresponding to a fixed value of the parameter $\rho c / \rho_W c_W$. 'ρ_W' and 'c_W' designating the mass density and the heat capacity of the wire material (i.e. of platinum). All the curvilinear lines have the same rectilinear asymptote, represemed by (7), transformed to the new coordinates.

To see how what has been mentioned immediately above can be used for the computation of λ we will assume that a blank experiment has shown that the current pulse does not disturb so that we can use the simple circuit analysis set forth in [2] as if the liquid were dielectric. Furthermore we will imagine that the bridge is in exact balance at t = 0, i.e. when the current is switched on. (The latter assumption does not, as explained in [2], mean a loss of generality). The circuit analysis set forth in [2], pages 38-47, then shows that the voltage φ registered on the recorder is directly proportional to the rise of T_W. Denoting that rise simply 'T_W', one has:

$$\varphi = \alpha T_W \quad , \tag{8}$$

where α is a proportionality factor which can be expressed as follows

$$\alpha = \frac{R_4}{\Sigma} R_W^o \beta I \quad . \tag{8a}$$

The meaning of the symbols (with reference to fig. 8) are

Σ = $R_W + R_2 + R_3 + R_4$

R_W (= R_C in [2], loc.cit) = the resistance of the hot wire

R_W^o = the resistance of the hot wire at the initial temperature

β = $\frac{1}{R_W} \frac{d R_W}{d T_W}$, corrected for thermoelastic errors as described in [2], section IV

I = the current flowing to the bridge.

I proved to be constant during measurements. Furthermore it has been demonstrated in [2] that for the modified apparatus one can use the initial value R_W^o for R_W in the expression for Σ, i.e. one can put

$$\Sigma = R_W^o + R_2 + R_3 + R_4 = \text{const}$$

during a measurement. Thus α in (8) is constant and the recorded voltage is proportional to T_W. It follows from the circuit analysis in [2] that 'Σ' in the above formula means the sum of all bridge resistances inclusive of supply resistances. According to the above only the wire resistance has a not-negligible supply resistance. The value of the wire resistance + its supply resistance was found by making the bridge balance with H_2O in the cell. That determination was repeated every time the cell had been taken apart for cleaning.

The wire resistance itself is only of interest for the control of "the level" mentioned in [2], page 60, and later on in the present work[9]. The reason is that the measurements were - as described shortly - relative and the value of the wire resistance itself drops out by this procedure.

As will be understood from the exposition of the method of calculation in [2], an accurate balancing adjustment before recording of diagrams is unnecessary. The diagrams may, as mentioned in connection with fig. 12, page 55 in [2], be differently displaced on the paper. To obtain a reasonable position a coarse balancing was performed with short pulses of current and the recorder pen as an indicator.

The curved line in fig. 10 will, if the ordinate is transformed from logarithmic to ordinary t-scale and the abscissa from T_W to $\varphi = \alpha T_W$, change into a curve K_{theor} - the theoretical curve. If this curve is drawn to a suitable scale, it will lie very close to the recorder diagram, i.e. to the recorded curve K_{rec}, but as certain corrections of K_{rec} (in principle at any rate) are necessary, it cannot coincide completely with K_{rec}. The

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[9] How the wire resistance itself was found is mentioned in [3], page 37.

corrections have been treated in [2], pages 47-55, and they originate in the following circumstances: The theoretical expression (17) of [2] giving the equation for K_{theor} presupposes 1) that the power q per unit length of the wire is constant during the measurement and 2) that the temperature field in the cell is strictly cylinder symmetrical as it would be if the wire were infinitely long and the liquid absolutely at rest. Furthermore, 3) the recorder has a certain inertia. This is a circumstance of a more practical kind and may also give rise to a correction. Since the wire resistance changes owing to heating during a measurement, q will not be exactly constant, but it turns out in [2], page 51, that the Ψ registrations are correct within 1% in spite of that source of error. Now, this is a rather small error but nevertheless it is too high. But as shown in [2] pages 26, 52 and 60 and in [3], section V, the error stemming from 1) and 2) are negligible if the measurement is carried out relative to a liquid with similar mechanical and thermal properties using the same period of registration for the two liquids. For that reason i.a. the measurements in the present work have been carried out relative to pure water and the electrolytic solutions have not been extremely concentrated. If one wants to measure on very concentrated solutions with the design chosen, one may measure relative to more and more concentrated solutions.

If one wants to measure absolute values of λ "directly" or to be able to measure on strongly concentrated solutions relative to water one should not use the full wire length for resistance measurements. The boundary problems at the wire ends (i.e. the source of error owing to presumption 2)) may be eliminated or made negligible by delimiting a region of the wire round its middle by thin potential leads and using only that region for the measurement. This way of improving the method has been mentioned in [2], page 22.

Furthermore it has been shown in [2], pages 52 f. that the error owing to 3) (the inertia of the recorder used at the semiautomatic stage) does not play any role.

According to the above we may now neglect the errors and imagine that the two curves $K_{rec.}$ and $K_{theor.}$, mentioned above, are identical. It is also a consequence of the above that if it is possible to find the slope $\frac{\Delta T_{as}}{\Delta \ln t}$ of the asymptote of the wire-temperature versus ln t graph from K_{theor} (K_{rec}), λ may be computed by

$$\left.\begin{aligned} \lambda &= \frac{q}{4\pi\Psi} \\ \Psi &= \frac{\Delta T_{as}}{\Delta \ln t} \end{aligned}\right\} \qquad (9)$$

As will be mentioned shortly an iterative method for finding Ψ from K_{rec} has been worked out. First it should, however, be said that on the basis of (9) it is shown in*) [2], page 56 that at an absolute measurement λ may be expressed by

$$\lambda = \frac{1}{4\pi} \frac{R_4 (R_W^0)^2 (R_2 + R_4)^2}{l \Sigma^3 \alpha \Psi} \beta I^3 , \qquad (10)$$

where

l = the length of the wire

α is given by (8a)

β = the resistance-temperature coefficient of the wire corrected according to [2], section IV.

in (10) the 'R''s refer to fig. 8 and I is as before the current from the source. If instead of a wire-temperature versus ln t diagram a recorder-voltage versus ln t diagram is considered one has with easily comprehensible symbols

$$\alpha\Psi = \frac{\Delta\Phi_{as}}{\Delta \ln t} = \Psi^* . \qquad (11)$$

If (11) is substituted into (10) the following is seen. If indices '1' and '2' refer to quantities measured at two experiments each with its liquid with λ values λ_1 and λ_2 respectively one has

$$\frac{\lambda_1}{\lambda_2} = \frac{S_1}{S_2} \cdot \frac{I_1^3}{I_2^3} \cdot \frac{\Psi_2^*}{\Psi_1^*} , \qquad (12)$$

where the 'S's are made up of symbols designating fixed resistances and resistances measured during the λ measurements. Hence, if one measures relatively, 'R_W^0', 'l' and 'β' disappear from the expression, and this is a considerable help because the said thermoelastic correction giving β exactly is difficult to find. Furthermore a very exact determination of the uncorrected β value is rather laborious. This is also a reason why the present author

*) In formula (64) loc.cit. there is a misprint. The formula should read '$\lambda = \frac{q_o}{4\pi\Psi}$', not '$\lambda = \frac{q_o \alpha}{4\pi\Psi}$'. Unfortunately the misprint has been repeated in [3], page 38. But the results in both [2] and [3] are correct.

chose to measure relatively.

From (10) and the meaning of the 'S's in (12) it is seen that the quantity

$$C = S\frac{I^3}{\Psi^5}\cdot\frac{1}{\lambda} = \frac{(R_2+R_4)^2}{\Sigma^3}\cdot\frac{I^3}{\Psi^*}\cdot\frac{1}{\lambda} \qquad (13)$$

is a constant determined by the apparatus at a given temperature, i.e. C is independent of the liquid with which the experiment is made. The quantity

$$C^* = \lambda C = \frac{(R_2+R_4)^2}{\Sigma^3}\,\frac{I^3}{\Psi^*} \qquad (14)$$

can be determined experimentally for a given liquid (at a given temperature). Naturally, it is not determined by the apparatus, but its introduction is convenient. If C^* is determined in experiments with H_2O at 20.00°C, a value

$$C^*_{H_2O} = \lambda_{H_2O} C \qquad (14a)$$

is found, and it is seen from the above that the thermal conductivity of a liquid relative to H_2O at 20.00°C can be calculated from

$$\lambda^* = \frac{\lambda}{\lambda_{H_2O}} = \frac{(R_2+R_4)^2}{\Sigma^3}\,\frac{I^3}{\Psi^*}\,\frac{1}{C^*_{H_2O}}\ , \qquad (14b)$$

where all the variables refer to the experiment with the said liquid. In the program for the computation of λ (at room temperature), $C^*_{H_2O}$ - determined experimentally at 20.00°C - is used as a fixed input value, and the computer calculates λ^*, which according to the above does not need any corrections owing to presumptions 1) and 2). Finally the computer multiplies λ^* by the most reasonable value for λ_{H_2O} at 20.00°C in the literature, and λ results. To this must be added that a check must be made to ensure that the two said corrections have reasonably small values in the H_2O experiment for determination of $C^*_{H_2O}$. If they are high, it can hardly be expected that the relative measurements on the electrolytic solutions will be correct when the corrections are omitted, unless only extremely diluted solutions are studied. However, it is easy to check that the "level" is correct with a reasonable accuracy. This check and its favourable outcome are mentioned in [2], page 60.

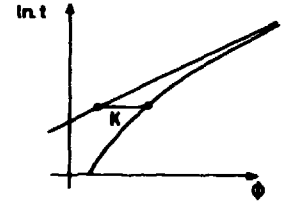


Fig.12

In the description of the λ computation now remains the mention of the iterative method by which the slope Ψ^* of the asymptote of a logarithmic recorder diagram is found. In fig. 12 the curved line indicates a recorder diagram transformed from ordinary t scale to a logarithmic one. It is seen that at a given t value a certain segment K must be subtracted from the voltage φ at t in order to arrive at a point of the asymptote at t. Graphically the procedure followed can be explained as follows: If λ, ρ, c and β (and thus also $\varkappa = \frac{\lambda}{\rho c}$) and the wire radius r_o were known the curved line on fig. 12 could be transformed into a corresponding curve on fig. 11 and the transformed K could be directly read in the latter figure. After this reading one could transform back to fig. 12. If this procedure were followed for a reasonable number of points (in principle for two only) the asymptote of fig. 12 would be known according to (8) and (8a). Now, ρ and c have for the solutions measured on been taken from the literature - and it turns out that extremely high accuracy is superfluous -. But λ is not known, it is sought. Nevertheless it turned out to be possible to follow an iterative procedure: After a rather short time (about 1.5 s) has elapsed from the moment t = 0 (i.e. from the switching on of the current) the curved line on fig. 12 is sufficiently rectilinear in the remainder of the measurement period to give a rough estimate of the desired slope of the asymptote. This estimate can be used as a first step in an iterative computation - using transformations and back-transformations - during which computations the segments K are determined with increasing accuracy.

What is described here, referring to diagrams in order to show the principle in a compact way, can also be done by calculations. During these β may be considered known, namely as the value for unstretched Pt taken from the literature. A small error in β only gives rise to a small error in the corrections sought and it does not matter in this context. Let

$$x = \frac{4\varkappa t}{r_o^2}\ ,$$

$$y = \frac{4\pi\lambda T_W}{q}\ ,$$

then Carslaw and Jaeger [6], p. 345 give the following approximation

$$y = -0.5772 + \ln x + \frac{2}{x} + \frac{2}{x}\left(1 - \frac{\rho_W c_W}{\rho c}\right)(\ln x - 0.5772) \qquad (15)$$

for the dimensionless curve corresponding to the curved line fig. 10. (Carslaw and Jaeger's formula is slightly more general than the mentioned one. Concerning the specialization used here, see [2], page 58). The approximative formula (15) is valid for high x values. Now N.E. Kaiser - who also most obligingly worked out the final code - introduced extra terms in the approximative formula in order to enlarge its range of validity. Kaiser's formula is as follows

$$y = -0.5772 + \ln x + \frac{2}{x} - \frac{1.5}{x^2} + \frac{2}{x}\left(1 - \frac{\rho_W c_W}{\rho c}\right)(\ln x - 0.5772)\left(1.05 - \frac{\ln x}{10}\right). \qquad (16)$$

How this formula was checked and found to be an extremely good approximation for

$$x \geq 5 \text{ and } \frac{\rho c}{\rho_W c_W} > 1$$

is described in [2], page 58. The latter condition is fulfilled for all the electrolytic solutions measured on, and the first one (i.e. $x \geq 5$) only means that one cannot use the very first registrations after the switching on of the current. Therefore all registrations made from 0 to 1.5 second have been cut away during all the measurements given in this work. As to the upper limit of the recording period some remarks will be made in the next subsection. Using Kaiser's formula it is evident that the procedure indicated above by referring to graphs can now be carried out by computation. As to the convergence of the iterative process it turned out that generally 2 or 3 steps were sufficient and the first λ-value was about 7% too high. These matters are described in [3], pages 43-44. On pages 41-43 of [3] is furthermore demonstrated that small systematic errors in ρ, c and r_o vanish during the iteration. This means that it has been possible to take ρ and c values for the solutions rather uncritically from the literature. By altering the values of ρ and c used as input this was confirmed: generally a change in $\rho \cdot c$ of 10% in one direction resulted in a change of the calculated λ of 1 - 1.5% in the opposite direction. Incidentally it follows from a parenthetic remark on page 23 of [2] that in principle it must be possible to alter the calculation method so as to give not only λ of the liquid but also its ρ and c. If the author's work had not been made limited in time

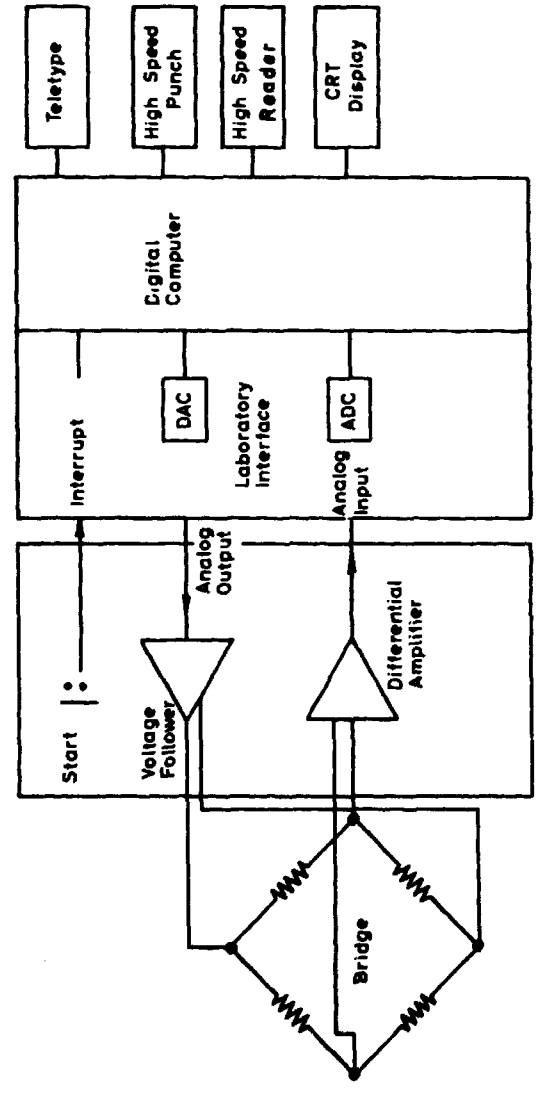


Fig 13

he would have investigated this possibility i.e. if ρ and c - or $\rho \cdot c$ - might be computed simultaneously with λ with reasonable accuracy by altering the calculation program. Furthermore he would have introduced the above-mentioned potential leads, using only a part of the wire for the registrations.

Finally the following should be mentioned concerning the experimental technique. Owing to the sources of error in the calculation of λ it was found that the time interval of the measurement and the current should be chosen approximately equal at the basic experiments with water for calibration (determination of C^* or C in (14) and (13)) and at the measurement on the liquid, the λ value of which shall be determined. If that condition is fulfilled the time interval itself plays - naturally within certain limits - no role. This has been mentioned in [3], pages 39-40.

b) Improvement of the Measurements by Introduction of Full Automation

As mentioned above the work was temporarily finished at a semiautomatic stage, the value pairs (φ, t) being taken from recorder diagrams by manual measuring out. That procedure was the basis of the work described in [2] and [3], and it was followed because the author had no suitable computer at his disposal. The mentioned pairs (φ, t) found manually were then - together with other necessary readings such as the current - used as inputs for a computer processing. However, full automation has now been possible and it has been carried out with the kind assistance of Frode Hansen, The Electronics Department of Risø.

The principle of the full automatic set-up is given by the block diagram, fig. 13. The bridge is the usual one for the apparatus modified for electrolytic measurements, i.e. it is of the type given with rounded values for the resistances as "Bridge II", fig. 8. The necessary exact measurements of the resistances are mentioned in [3], pages 36-37. The abbreviations used on the block diagram are the usual ones:

D A C = Digital Analog Conversion
A D C = Analog Digital Conversion
C R T = Cathode Ray Tube.

The maximum voltage given by the digital computer is 10 volt and its resolution is $10 \cdot 10^{-3}$ volt. The amplification factor of the voltage follower is 1.0000. Measurements were taken with an interval of $30 \cdot 10^{-3}$ second and in accordance with what was said in the previous subsection the first 50 registrations were cut away in order to make the approximation (16) valid. The current to the bridge was - as before - about 3.6 A. After a short period

in which noise problems etc. were studied in collaboration with The Electronics Department of Risø this set-up turned out to be an essential improvement. Now experiments could naturally be carried out much more quickly than at the semiautomatic stage and a closer investigation of i.a. the upper limit of the measuring period could easily be undertaken by varying the number of registrations in a comprehensive set of experiments. According to section II the convection in the measuring cell does not disturb the heat transport through the liquid as long as it is laminar, but after a certain elapse of time it will be turbulent. In [3], pages 46-47 some investigations are sketched, showing that below about 10 second after the switching on of the current one may expect the convection to be laminar for the electrolytic solutions (and H_2O). At the semiautomatic stage experiments not strictly necessary were omitted because of the laborious procedure and the upper limit was therefore usually chosen to be about 8 second in order to be on the safe side. But now a series of experiments showed that it was safe enough to choose 10 - 10.5 second, which gives more points and therefore improves the statistics of the method. Therefore 300 - 50 = 250 or 350 - 50 = 300 registrations were used at the full automatic stage. As will be seen from the following subsections the improvement by changing to full automatic apparatus - apart from the increased quickness of the procedure - can best be described by mentioning that the standard error of the results is changed from about 1 - 1.5% to about 0.2 - 0.5%.

c) Results of the Experiments

1. Determination of the Quantity $C^*_{H_2O}$ Defined by (14) and (14a), Page 40

According to the description of the calculation method in subsection a), the value of $C^*_{H_2O}$ defined on page 40 must be determined first and foremost. This is done by filling the cell with redistilled water and measuring (φ, t)-value pairs with the fixed current I (e.g. 3.7 A) and the fixed time interval Δt chosen for the λ measurements ($1.5 \text{ s} < \Delta t < 10.5 \text{ s}$). Fig. 14 is a reproduction of the recorder diagram from such an experiment at the semiautomatic stage and it is reduced to half size. 'l' in the text to the figure designates the wire length. In [3], pages 44-45 the way of determining $C^*_{H_2O}$ is described in more detail. At the semiautomatic stage 2 series of 10 individual measurements were carried out showing standard errors 0.34% and 0.35% for the two means of $C^*_{H_2O}$. These standard errors were calculated directly by the computer using the usual formula for that quantity. Thus, at the semiautomatic stage, the mean of the means of the series could - on the presumption of gaussian

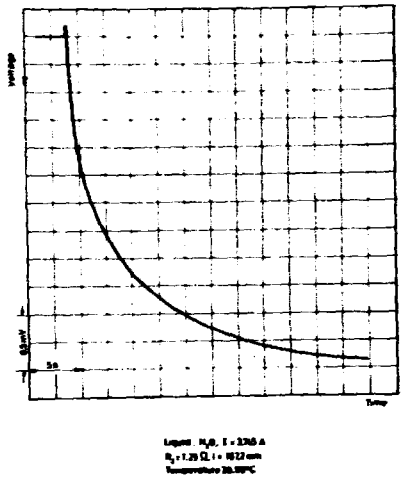


Fig. 14

distribution - be given with a standard error of about 2.5 o/oo which was considered negligible as compared to the mentioned standard error of the λ values (1 - 1.5%) when the code was worked out.

At the full automatic stage 3 series of each 10 individual measurements were carried out for the determination of $C^*_{H_2O}$, showing the following standard errors of the means: 0.07%, 0.08% and 0.07%. Hence using the mean of the 3 means $C^*_{H_2O}$ can, on the above-mentioned presumption, be given with the standard error 0.4 o/oo, which is also negligible as compared to the standard error obtained for the λ values measured (about 4 o/oo for single determinations). The value of $C^*_{H_2O}$ is of minor importance in the present context because it was determined every time the cell had been taken apart for cleaning or when a new wire was inserted (because the wire retainers had damaged the old one). $C^*_{H_2O}$ therefore varied slightly during the experiments but the mentioned standard errors of the means always held good. The value of $C^*_{H_2O}$ was also controlled regularly during the measurement series, i.e. not only at a change of wire. A typical value of $C^*_{H_2O}$ was

$$C^*_{H_2O} = 1.9652 \cdot 10^4 \text{ W } \Omega^{-3} \text{ at } 20.00^\circ\text{C} \ .$$

The reason why this value is not in accordance with the value given in [3], page 45 for the semiautomatic experiments is that a mishap made it necessary to replace two of the resistances in the bridge at the outset of the full

automatic experiments. The new resistances turned out to have new values (when measurtd out at 20.00°C with a Müller bridge).

2. "Blank Experiments" on the Chosen Electrolytic Solutions

On pages 12 ff a "blank experiment technique" for revealing disturbances during the measurements owing to the current pulses in the solutions was described. The platinum hot wire is, during such blank experiments, replaced by a manganin wire with the same resistance. At such experiments no changes in the wire resistance caused by heating occur and only electrical disturbances, if any, are registered. Figures 4 and 5, page 15 show the results of two typical blank experiments, one in a "classical" and the other in a "modified" set-up and the distinction between them is obvious. Such blank experiments were carried out on all the solutions studied in the present work using the recorder from the semiautomatic set-up. It turned out that the diagram shown in fig. 5 is so characteristic for all the experiments that there is no reason for reproducing all the "blank curves". Furthermore - as shown in [3] - this means that no disturbances of any importance of electrical origin have been present during the λ measurements mentioned in the next subsection of the present subsection c).

Although no measurements on very concentrated solutions are given below, it should be mentioned here that blank experiments were carried out on some such solutions, e.g. on about 20 N NaOH. Such blank curves also turned out to be completely satisfactory. Hence the method works in principle for strongly concentrated solutions as well as for the ones measured on. The only reason for not giving λ values for strongly concentrated solutions is that the design chosen presupposes - as mentioned on page 38 - that the mechanical and thermal properties of the solution measured on do not deviate too much from those of H_2O, if the apparatus is calibrated by means of water, as has been the case during the present work. If the possibility mentioned on page 38, namely using thin potential leads for delimiting a piece of wire around the middle of the wire *) is implemented, measurements can be made on ordinary electrolytic solutions in any concentration. However, for practical reasons the author had no possibility of doing this.

*) The circuit would then be slightly more complicated.

3. Measurements of λ Values for Some Aqueous Electrolytic Solutions at Room Temperature

In the following the results of the measurements are given in tables and diagrams, and finally they are discussed. All chemicals from which the aqueous solutions were prepared were analytical reagents. A. Thorboe of the Chemistry Department at Risø kindly had the solutions prepared and analysed. In the tables 'N' means the normality of the solutions. ρ and c are mass densities and specific heats respectively. 's' means standard error and 's_n' standard error of the mean of n measurements, both s and s_n being given as % of λ. At the semiautomatic stage it was chosen to determine λ as the mean of 10 measurements (n = 10), but with the full automatic set-up it turned out experimentally that 5 measurements (n = 5) were quite sufficient. The mean of 5 measurements did not deviate appreci-

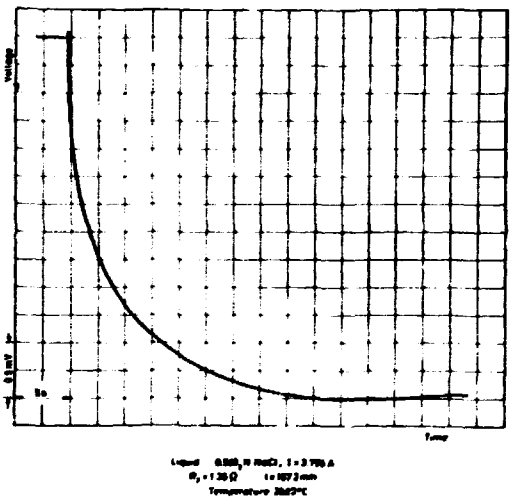


Fig. 15

ably from the mean of 10 measurements.

Fig. 15 is a tracing reduced to half size of a characteristic recorder diagram from the measurements on electrolytic solutions at the semiautomatic stage. It gives an impression of the development of the registered voltage in time. The marked change in direction at about 30 second after the switching on of the current is caused by turbulence, but turbulence sets in before, i.e. the curve is altered by turbulence before a period of 30 second has elapsed (cf [3], pages 46-47).

The tables and diagrams comprise measurements on 76 aqueous solutions of 14 different inorganic electrolytes, each in different concentrations, at room temperature measured either with the semiautomatic or the full automatic device (or with both). To the numbers of the tables have been added 's''s as subscripts when they refer to semiautomatic measurements, and such tables have been reproduced from [3], section V. In the diagrams showing the measurements with the full automatic set-up have been plotted values marked 'L-B' for comparison with measurements found in the literature. The "L-B-values" will be mentioned later on.

The reason why the straight lines in the diagrams from the full automatic measurements pass exactly through the points (N, 10λ) = (0, 6.00), and the lines from the semiautomatic measurements do not, is given in the discussion, *section IV*.

The electrolytes investigated are:

Salts (tables I_s - VII_s):
$NaCl$, Na_2SO_4, KCl, KBr, KNO_3, K_2CO_3, $CuSO_4$

Bases (tables VIII - XII):
NH_3, $LiOH$, $NaOH$, KOH, $CsOH$

Acids (tables $XIII_s$ - XIV):
H_2SO_4, HNO_3.

The reason why HCl has been omitted among the acids is given on page 16.

The ρ and c values were - in accordance with remarks page 42 found by means of the standard works Landolt-Börnstein, Physikalisch-Chemische Tabellen, Gmelin's Handbuch der anorganischen Chemie and the CRC Handbook of Chemistry (53 ed. 1972-1973). Where necessary the concentration units were converted into normality, and interpolation and extrapolation were used in the tables of the mentioned works. By comparisons, the values that seemed to be the most reliable were chosen. The said remarks, page 42 show that ρ and c need not be known with very high accuracy, and the values found must be considered fully

adequate. The only two cases which may - perhaps - beforehand be said to be slightly dubious are the values for the $CuSO_4$ and CsOH solutions. As to the $CuSO_4$ solutions, which are only measured with the semiautomatic device - i.e. with "small" accuracy - the possible error in c, which is mentioned in [3], page 50, hardly matters. As to the CsOH solutions no values were found at all, but the solutions were all rather diluted and - taking the permissible inaccuracy of $\rho \cdot c$ into consideration - it was considered sufficient - although not strictly correct - to use the corresponding values for KOH solutions. As a "justification" for this the λ values of the CsOH solutions were also computed by using $\rho \cdot c$ for H_2O as input values, and it was assumed that the difference of $\rho \cdot c$ between H_2O and KOH solutions would not be numerically (much) higher than the difference of $\rho \cdot c$ between KOH and CsOH solutions. Using ρc for water instead of for KOH solutions the λ value of the strongest CsOH solution (0.5 N) did not change.

For the full automatic measurements the accuracy of the ρ and c values is of course more important than for the semiautomatic ones. As a matter of fact the ρ values used as inputs for the full automatic experiments were taken (from the CRC-handbook) with a decimal that has - for the sake of uniformity in the tables - not been given in the following. It hardly matters.

As to the bases, they were measured on as soon as they were received from the Chemical Department of Risø in order to exclude as far as possible CO_2 absorbtion from the air in the bottles.

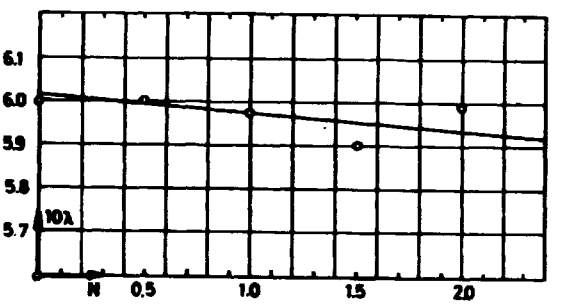
On the following pages are given the mentioned tables and diagrams.

Table I_s

Measurements on aqueous NaCl solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.503	1020	4033	6.01	1.26	0.40
1.010	1040	3911	5.97	0.60	0.19
1.510	1060	3803	5.90	1.31	0.41
2.009	1080	3695	5.99	0.92	0.29

Fig. 16 shows the measurement results from table I_s in graphical representation.



Measurements on NaCl solutions from table I_s

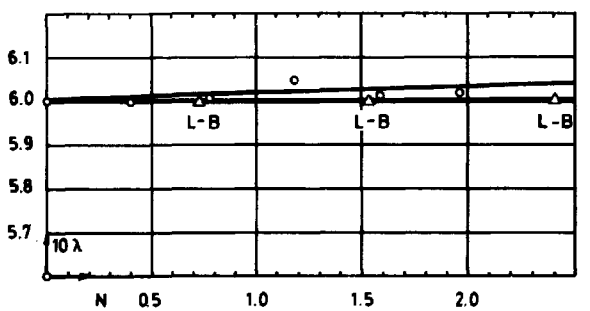
Fig. 16

Table II

Measurements on aqueous Na_2SO_4 solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.392	1022	4042	6.00	0.26	0.11
0.780	1047	3910	6.01	0.12	0.05
1.183	1070	3745	6.05	0.32	0.14
1.580	1093	3721	6.02	0.35	0.16
1.962	1115	3698	6.03	0.63	0.28

Fig. 17 shows the measurement results from table II in graphical representation. Own measurements are marked by circles.



Measurements on Na_2SO_4 solutions from table II

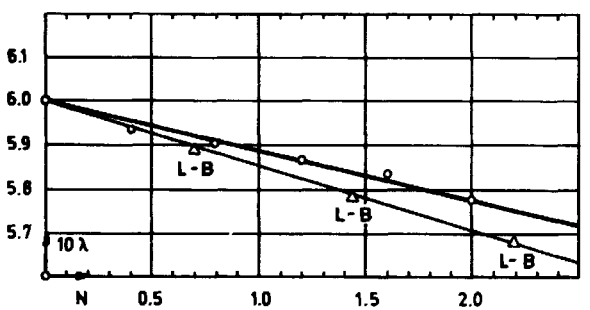
Fig. 17

Table III

Measurements on aqueous KCl solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.400	1017	4036	5.94	0.45	0.20
0.798	1035	3905	5.91	0.17	0.07
1.203	1053	3770	5.87	0.26	0.12
1.602	1071	3650	5.84	0.31	0.15
1.999	1091	3532	5.78	0.28	0.12

Fig. 18 shows the measurement results from table III in graphical representation. Own measurements are marked by circles.



Measurements on KCl solutions from table III

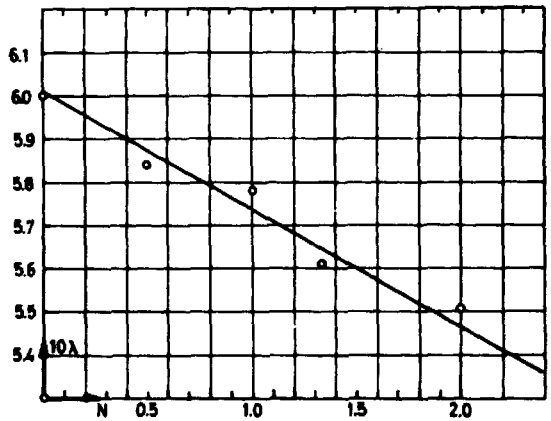
Fig. 18

Table IV_s

Measurements on aqueous KBr solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.502	1040	3893	5.84	1.02	0.32
1.010	1080	3684	5.78	0.83	0.26
1.341	1107	3571	5.61	1.02	0.32
2.013	1160	3349	5.51	1.88	0.60

Fig. 19 shows the measurement results from table IV_s in graphical representation.



Measurements on KBr solutions from table IV_s

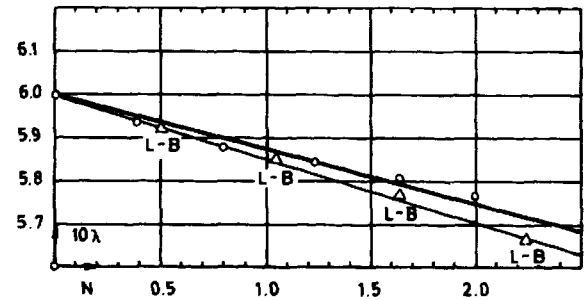
Fig. 19

Table V

Measurements on aqueous KNO_3 solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.405	1023	4013	5.94	0.10	0.04
0.796	1047	3862	5.88	0.25	0.11
1.227	1073	3727	5.84	0.38	0.17
1.637	1096	3595	5.81	0.31	0.14
2.005	1118	3492	5.77	0.26	0.12

Fig. 20 shows the measurement results from table V in graphical representation. Own measurements are marked by circles.



Measurements on KNO_3 solutions from table V

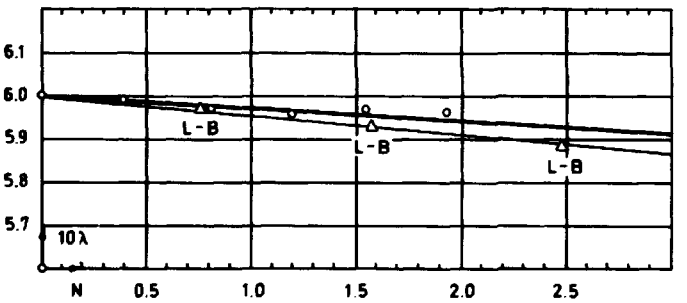
Fig. 20

Table VI

Measurements on aqueous K_2CO_3 solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	s_5 %
0.388	1022	4050	5.99	0.17	0.08
0.791	1046	3937	5.97	0.35	0.15
1.188	1068	3824	5.96	0.22	0.10
1.547	1088	3712	5.97	0.19	0.08
1.926	1110	3589	5.96	0.29	0.13

Fig. 21 shows the measurement results from table VI in graphical representation. Own measurements are marked by circles.



Measurements on K_2CO_3 solutions from table VI

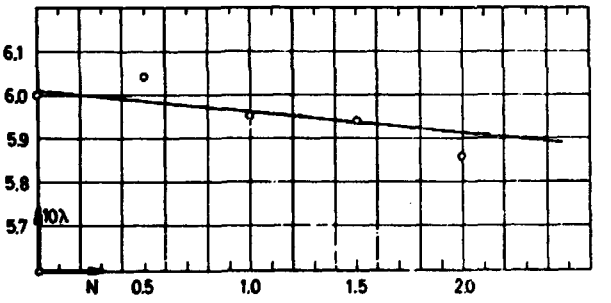
Fig. 21

Table VII_s

Measurements on aqueous $CuSO_4$ solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	s_{10} %
0.509	1039	3999	6.04	1.87	0.59
1.005	1078	3700	5.95	1.28	0.41
1.504	1116	3553	5.94	1.25	0.39
2.018	1154	3551	5.86	0.61	0.19

Fig. 22 shows the measurement results from table VII_s in graphical representation.



Measurements on $CuSO_4$ solutions from table VII_s

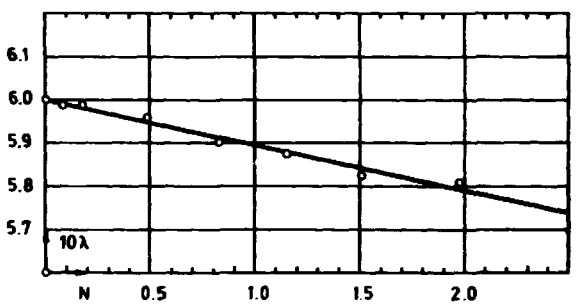
Fig. 22

Table VIII

Measurements on aqueous NH_3 solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	s_5 %
0.089	998	4181	5.99	0.23	0.10
0.175	997	4176	5.99	0.27	0.12
0.493	995	4157	5.96	0.11	0.05
0.831	992	4137	5.90	0.17	0.08
1.149	989	4156	5.87	0.26	0.12
1.508	987	4180	5.83	0.25	0.11
1.979	983	4191	5.81	0.10	0.04

Fig. 23 shows the measurement results from table VIII in graphical representation.



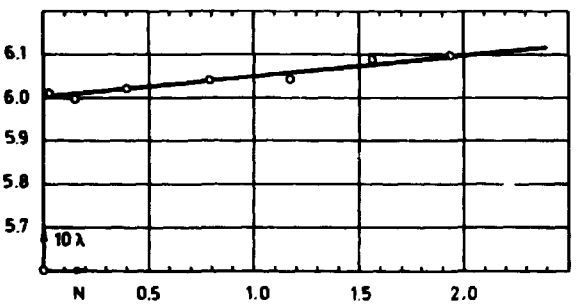
Measurements on NH_3 solutions from table VIII
Fig. 23

Table IX

Measurements on aqueous LiOH solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	s_5 %
0.018	1000	4175	6.01	0.33	0.15
0.154	1002	4160	6.00	0.22	0.09
0.391	1008	4123	6.02	0.37	0.16
0.788	1019	4065	6.04	0.21	0.10
1.174	1028	4035	6.04	0.47	0.21
1.560	1037	4016	6.09	0.18	0.08
1.941	1047	4005	6.10	0.28	0.13

Fig. 24 shows the measurement results from table IX in graphical representation.



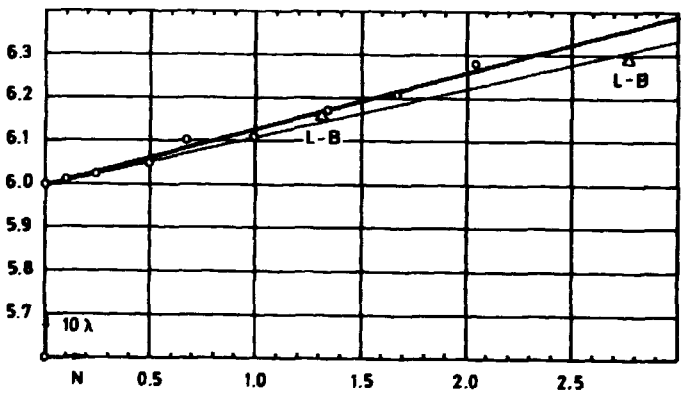
Measurements on LiOH solutions from table IX
Fig. 24

Table X

Measurements on aqueous Na OH solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.101	1004	4161	6.01	0.31	0.14
0.251	1010	4124	6.02	0.25	0.11
0.504	1020	4060	6.05	0.47	0.21
0.672	1027	4028	6.10	0.14	0.07
1.012	1042	3976	6.11	0.36	0.16
1.338	1054	3926	6.17	0.33	0.15
1.669	1068	3888	6.21	0.49	0.22
2.047	1081	3850	6.28	0.29	0.13

Fig. 25 shows the measurement results from table X in graphical representation. Own measurements are marked by circles.



Measurements on NaOH solutions from table X

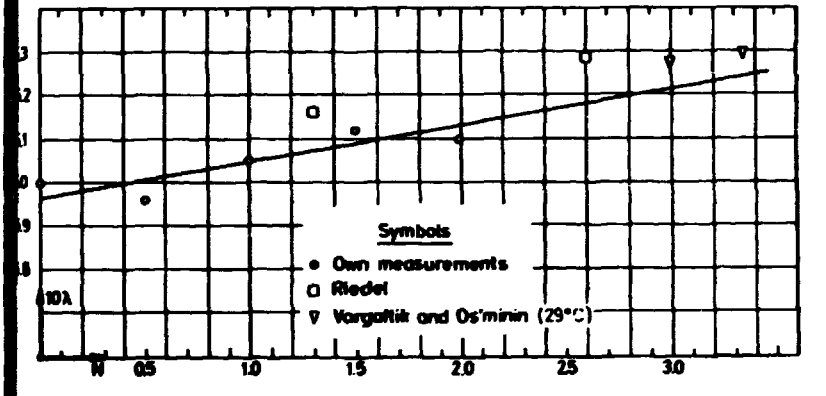
Fig. 25

Table X_s

Measurements on aqueous Na OH solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_{10} %
0.500	1020	4062	5.96	1.06	0.34
0.999	1041	3975	6.05	0.85	0.27
1.496	1060	3914	6.12	1.85	0.58
1.985	1080	3852	6.10	1.00	0.32

Fig. 26 shows the measurement results from table X_s in graphical representation.



Measurements on NaOH solutions from table X_s

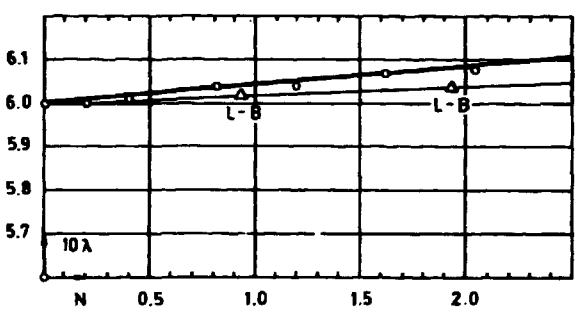
Fig. 26

Table XI

Measurements on aqueous KOH solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.200	1008	4111	6.00	0.55	0.25
0.401	1018	4032	6.01	0.24	0.11
0.815	1035	3922	6.04	0.44	0.20
1.217	1055	3825	6.04	0.09	0.04
1.626	1074	3723	6.07	0.20	0.09
2.045	1092	3630	6.08	0.08	0.04

Fig. 27 shows the measurement results from table XI in graphical representation. Own measurements are marked by circles.



Measurements on KOH solutions from table XI

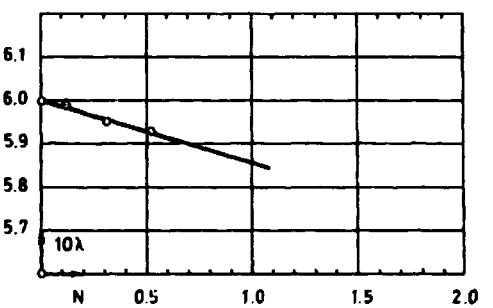
Fig. 27

Table XII

Measurements on aqueous CsOH solutions at 20.00°C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,{}^{o}C^{-1}$	10 λ $Wm^{-1}\,{}^{o}C^{-1}$	s %	s_5 %
0.106	The corresponding values		5.99	0.27	0.12
0.305	for KOH solutions have		5.95	0.28	0.13
0.511	been used. See comments		5.93	0.26	0.12
	on page 50.				

More concentrated solutions were not at the author's disposal. Fig. 28 shows the measurement results from table XII in graphical representation.



Measurements on CsOH solutions from table XII

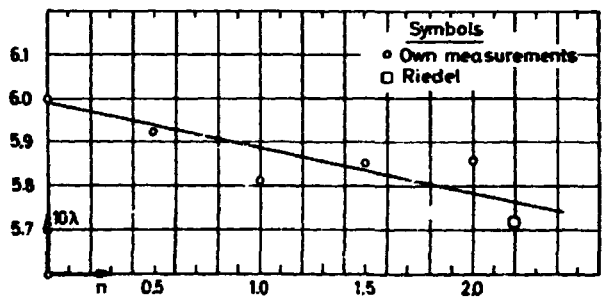
Fig. 28

Table XIII$_s$

Measurements on aqueous H_2SO_4 solutions at 20.00 °C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	s_{10} %
0.505	1015	4081	5.92	0.54	0.17
1.007	1030	3998	5.81	1.86	0.59
1.507	1046	3914	5.85	0.71	0.23
2.013	1061	3880	5.86	1.18	0.37

Fig. 29 shows the measurement results from table XIII$_s$ in graphical representation.



Measurements on H_2SO_4 solutions from table XIII$_s$

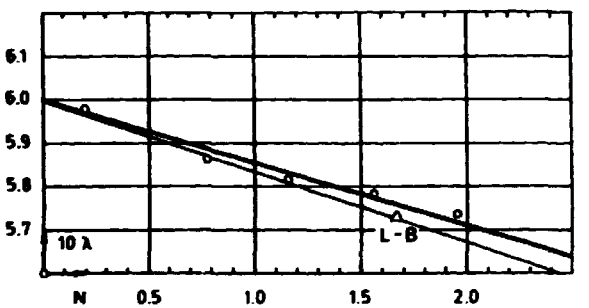
Fig. 29

Table XIV

Measurements on aqueous HNO_3 solutions at 20.00 °C

N equil. l^{-1}	ρ kgm^{-3}	c $J\,kg^{-1}\,°C^{-1}$	10 λ $Wm^{-1}\,°C^{-1}$	s %	$s_{\bar{5}}$ %
0.200	1005	4130	5.98	0.22	0.11
0.776	1025	3960	5.87	0.32	0.14
1.155	1037	3855	5.82	0.62	0.28
1.557	1050	3743	5.78	0.16	0.07
1.945	1063	3620	5.74	0.41	0.20

Fig. 30 shows the measurement results from table XIV in graphical representation. Own measurements are marked by circles.



Measurements on HNO_3 solutions from table XIV

Fig. 30

IV. Discussion of the Measurement Results

For the planning of the experiments the purpose of the investigation was, of course, decisive. In the course of the work the purpose was, however, altered.

The work was prompted by an inquiry from Danish industry (1956) to the Danish Atomic Energy Commission Research Establishment Risø. The establishment received samples of liquids, and the inquirer desired their thermal conductivity measured with an apparatus built for "classical" hot-wire measurements on organic reactor coolants (by the author). The measurements asked for turned out to be impossible because the samples proved to be electrolytically conductive. It was therefore obvious to try to modify apparatus and method so that measurements could be made on electrolytic solutions as well as on dielectric liquids. Hence, at the first stage what was aimed at was a modification of the method permitting in a simple way (cf. the extension of the electrically insulating layer round the wire, giving rise to theoretical and practical difficulties) to measure λ values of electrolytic solutions with an accuracy which was sufficient for technical purposes. That accuracy was estimated to be $\pm$ a few per cent. When the initial, coarse, theoretical deliberations were finished and the first version of the set-up was built, it became clear that it would without difficulty - using mainly components immediately available - be possible to obtain an accuracy of about $\pm$ 1%.

When that was obtained with the semiautomatic set-up, described in [3], the composite work [28] (1959) had been published. That work is written by many experts in λ measurements, and from the preface to it it was seen that the demands seemed to be $\pm$ 10% for engineering purposes and $\pm$ 2% for basic studies, with the addition that these claims will soon be replaced by more severe ones. Since λ measurements are certainly important for basic studies such as confirmation of existing statistical-thermodynamical theories (diluted systems) and possible future ones, and since it seemed that the accuracy obtained by the author was - or was not far from being - sufficient for basic studies, the demands on the set-up were increased. Furthermore it must be important for basic studies to be able quickly to make series of routine measurements and at that same time a suitable computer for full automation became available. These circumstances determined the purpose of the present work, which is meant as an improvement of [2] and [3].

According to the above small print text the final purpose has been: Development of a full automatic modification of the method so that λ can be measured at a given temperature for an electrolytic solution with given composition and with a standard error of about 5 o/oo or less together with a theoretical treatment which ensures that the systematic errors are reasonably small.

As to the statistical aspects of the λ determinations it seems reasonable to assume that the results are gaussian distributed during repetitions as the measurements are composed of well-known, elementary laboratory operations such as readings of the temperature in a thermostat, of currents,

resistances, voltages, and slopes of curves in a, in a certain sense, rather "ordinary" set-up. At the full automatic stage it would have been possible to make so many repetitions (presumably at least 100) of single determinations that reliable χ^2 tests could be performed. But small deviations from gaussian distribution will hardly be of any importance for the s_n's, computed as $s_n = \frac{s}{\sqrt{n}}$, and for the subsequent reasoning. χ^2 tests were in accordance with these remarks considered superfluous.

Now, assuming gaussian distribution, and p_1, p_2, p_3 ... being the readings during a measurement, one has as the best estimate

$$10^{-2}\lambda\, s = \sqrt{\left(\left(\frac{\partial\lambda}{\partial p_1}\, s_1\right)^2 + \left(\frac{\partial\lambda}{\partial p_2}\, s_2\right)^2 + \dots\right)}, \qquad (17)$$

where s_1, s_2, s_3 ... are the standard errors of p_1, p_2, p_3 ... . Among the latter is the temperature T, the normality N, and the calibration constant $C^*_{H_2O}$ with the standard errors s_T, s_N and s^*. If the sum of the contributions from the other s's under the square root sign is put equal to Σ, one thus has

$$10^{-2}\lambda\, s = \sqrt{\left(\Sigma + (\lambda_T\, s_T)^2 + (\lambda_N\, s_N)^2 + (\lambda_{C^*_{H_2O}}\, s^*)^2\right)},$$

where the subscripts to the 'λ''s mean partial differentiations. Since the demand is that s = 0.5 we have

$$25 \cdot 10^{-6} = \frac{\Sigma}{\lambda^2} + \left(\frac{\lambda_T\, s_T}{\lambda}\right)^2 + \left(\frac{\lambda_N\, s_N}{\lambda}\right)^2 + \left(\frac{\lambda_{C^*_{H_2O}}\, s^*}{\lambda}\right)^2 . \qquad (18)$$

By examination of the tables in "Landolt-Börnstein" II Band, 5 Teil, pages 91 f giving λ values for aqueous electrolytic solutions it is found that the order of magnitude of $\frac{\lambda_T}{\lambda}$ at room temperature is roughly

$$\frac{\lambda_T}{\lambda} \simeq 3 \cdot 10^{-3}\ {}^{o}C^{-1}.$$

As mentioned earlier the temperature could be determined - by resistance thermometers - with an accuracy of $\pm$ 0.02 °C. Substituting this and the value of $\frac{\lambda_T}{\lambda}$ into (18) it is found that the contribution to s from s_T is completely negligible.

A glance at the tables or diagrams of the present work, or use of the mentioned Landolt-Börnstein tables, shows that one may in the most unfavourable case (KBr) put

$$\left|\frac{\lambda_N}{\lambda}\right| \simeq 3 \cdot 10^{-2}\ 1 \cdot \text{equil}^{-1},$$

so that the contribution from s_N in (18) is $< 9 \cdot 10^{-4} \cdot s_N^2$ or, if s_N is x% of N, $< 9 \cdot 10^{-4} \cdot 10^{-4} N^2 \cdot x^2$. Since $N \neq 2$ in the investigations, the mentioned contribution is $< 40 \cdot 10^{-8} \cdot x^2$. If only $x < 1$, which can rather easily be obtained by the chemical analyses, the contribution from s_N to s is also negligible.

Finally it is seen from the remarks on page 46 that $C^*_{H_2O}$ can rather easily be determined so accurately that the contribution to s from s^* is also negligible, and hence it turns out that the temperature measurement, the chemical analyses, and the calibration do not contribute to the standard error of the λ determination. This must be a reasonable demand on the planning of measurements to fulfil the mentioned purpose.

A glance at the previous tables shows that s - the standard error in per cent of a single determination computed directly from computed λ values, i.e. without using (17) and estimates of the s's of the remaining p's - turned out to be very satisfactory. For the semiautomatic device s was 1 - 1.5% and for the full automatic one 0.2 - 0.5%. This, together with the fact that the T , N and $C^*_{H_2O}$ determinations did not contribute to s is the statistical main result of the present investigation. The determinations of $C^*_{H_2O}$ generally turned out to give slightly better s values. This is tantamount to measurements on dielectric liquids being slightly more accurate or, in other words that, after all, the electrical conductivity of the solutions increased the random errors a bit. But the very small s values for the solutions show that this is of no importance.

As to the systematic errors - in so far as they are sharply distinguishable from the random ones - it is more difficult to give an estimate. In principle it ought to be possible to give quantitative corrections for them through an elaborate, theoretical investigation of the set-up. Such an analysis has been carried through to a certain extent in [2], [3] and [4]. An estimate on the basis of these investigations must - in the opinion of the author - be that the systematic error is of the same order of magnitude as s or less, i.e. < 0.5%: In [2], page 26 and pages 48-54 were treated the systematic errors at relative measurements on dielectric liquids with the semiautomatic set-up, and in [3], pages 38 f the discussion was deepened. Discussions with the Electronics Department of Risø made it probable that the change from recorder to full automatic set-up with the specifications given on page 44 would not alter the systematic errors. The said investigations in

[2] and [3] make it highly probable that the relative method using the same period of measurement during calibration and λ measurements only gives rise to errors of a few o/oo if the mechanical and thermal properties of the basis liquid (H_2O) and the liquid to be measured on are not too different. In [3], section III - the theoretical foundation of which has, in its turn, been elaborated and justified in [4] - it is shown that the change from dielectric liquids to electrolytic solutions does not cause an increase of the systematic errors if blank experiments show that one is on the safe side, as they have done for all the measurements given in the tables of the present work. The rather vague condition that "the mechanical and thermal properties must not be too different" can, as mentioned, be eliminated by using potential leads for delimiting a wire piece round the middle of the wire, but practical circumstances made it impossible to implement that possibility of refinement. The "direction" of the systematic errors can hardly be deduced from the mentioned analyses, but it seems highly probable that they give slightly too high results. This will be mentioned later on.

Another way of trying to estimate the systematic errors is to compare the results with values found in the literature, which have, in the nature of the case, been obtained by other methods. For such a comparison to be meaningful it must be possible to give a reasonable criterion for two measurements of the same qusntity by different methods being compatible or incompatible. This is a well-known problem treated in textbooks on measurement technique. Here we may use some remarks in [21], page 46.

Let s_1 be the standard error of λ measured by another method and $s_2 = 10^{-2}\lambda$ s the standard errors corresponding to the s values given in the tables of the present work. Now, a certain difference $d = |s_1 - s_2|$ is permissible before the corresponding λ values, λ_1 and λ_2, must be considered incompatible. The "other" method may, as well as the present one, be supposed to give results that are gaussian distributed. The standard error of d, s_d is then given by

$$s_d \simeq \sqrt{\left(s_1^2 + s_2^2\right)},$$

(which would be exactly valid if the s's were standard deviations). Now, many of the data given in the literature are older ones, and according to the estimates in [28], mentioned on page 66 with regard to the accuracy of λ measurements demanded for basic studies (1969) we may e.g. put

$$\frac{10^2 s_1}{\lambda} \approx 2$$

and neglect s_2 for the full automatic set-up. Hence

$$s_d \simeq 2 \cdot 10^{-2} \lambda \simeq 2 \cdot 10^{-2} \cdot 0.6 \text{ W m}^{-1} \text{K}^{-1}$$

or

$$s_d \simeq 1.2 \cdot 10^{-2} \text{ W m}^{-1} \text{K}^{-1}.$$

According to [21], page 46 one would not declare λ_1 and λ_2 incompatible before

$d \geq 2 s_d$, if $d \neq 0$ is due to random errors only.

($d = 2 s_d$ corresponds to the probability of the value of d being only 4.5%). Now, let

$$\frac{10^2 d}{\lambda} = \tau .$$

Clear-cut incompatibility then requires

$$10^{-2} \lambda \tau \simeq 10^{-2} \, 0.6 \tau \geq 2.4 \cdot 10^{-2} \text{ W m}^{-1} \text{K}^{-1}$$

i.e.

$$\tau \geq 4 .$$

For the semiautomatic set-up we may roughly put $s_1 = s_2$, which gives

$$\tau \geq 5.6$$

or less because the standard error on a single determination at the semiautomatic stage was $< 2\%$. Furthermore the s_2's given in the tables marked with 's''s are means of 10 measurements. Roughly one may therefore reckon with differences between values from the literature and own values that are about 4% of λ being sufficient in both cases to ensure compatibility, if the λ values from the literature are accurate within $\pm$ 2%*). But whether they really are, is an open question in cases where the works are not quite up-to-date. Here we may recall the "pessimistic" deliberations in the preface to the composite work [28] from 1969 quoted in [2], page 61 and concluding that "confusion" prevails within the field. In the work [25] by Strausmann from 1960 are plotted values from the earlier literature concerning dielectric liquids, and from his diagrams one reads e.g. differences which are 16% for ethyl alcohol and 9% for glycerol at 20°C. If one goes back to 1948 Riedel [23], page 21 says that an "an sich notwendiger" comparison of his results with other investigations does not bring "viel Neues".

*) Here it is assumed that systematic errors may be disregarded during the comparison.

He only mentiones values measured by Bridgman (1923) that seem to be 10% too high and other examples of differences being of the order of magnitude of 5%. Since then Riedel has - as will be mentioned shortly - made comprehensive and careful work concerning evaluation of the λ values found in the literature which has improved the situation somewhat. But he still (in 1968) says that deviations of 5% are common.

Remarks in the literature of the kind quoted, especially those from [28] (1969), makes it, to a certain degree, problematic if comparisons with the results of other researchers is a reliable way to study the systematic errors. This is the main reason why the present author has tried to give an elaborate theoretical treatment (especially in [4]) in support of his measurements. If systematic comparisons should be undertaken the methods with which comparisons were made had to be studied in detail, and their standard errors had to be judged. The comparisons have therefore in the present work been limited to the following.

If e.g. Alas' work [1]*) from 1967 is considered up-to-date, one may ascribe a reasonable weight to the comparisons with that work given in [3], page 59 for KBr , NaCl and $CuSO_4$ solutions. These comparisons refer to the present author's semiautomatic measurements. The highest difference found is 1.0% and the lowest is 0.2%. Since Alas gives (page 33, loc.cit.) as his accuracy $\pm$ 1%, it must be in agreement with the above considerations concerning compatibility to declare the measurements compatible. Alas compares his own values for all his measured salt solutions with those of other authors. As to Riedel's values he says that in some cases there is excellent agreement, and that in some cases the deviation is high (for $CaCl_2$ Alas finds values 1% higher than Riedel, and for KF Riedel's values are 1-2% higher than Alas's). Alas also quotes measurements made by Braune. Only in a few cases do they agree well with his own, and generally the deviations are higher than those from Riedel's values. Finally Alas states that measurements by Kapustinsky and Ruzavin are generally 1% above his own smoothed-out curves.

In accordance with the above it seemed desirable to systematize the comparisons with the literature when the full automatic measurements were finished, and the author chose to use the values given in the "Landolt-Börnstein tables" (II Band, 5 Teil, pages 91 f) from 1968 as

*) Here it should be mentioned that the author of [1] gives his name as 'Alberto Chiquillo Alas' and that the present author has referred to him by the name 'Alas'. However, it seems that in the literature, e.g. in [27], 1970, he is quoted under the name 'Chiquillo'.

standard values for comparison. These values are, as indicated, plotted in the diagrams with the signature 'L-B'. In the extremely comprehensive work [27] on thermal data, being under running edition, values for electrolytic solutions have not yet been included. Up to the last volume (1973) "electrically conductive liquids" only comprise liquid metals. Furthermore "Chemical Abstracts" and "Physics Abstracts" from 1969 up to mid-1973*) have been consulted using the keywords 'thermal conductivity or thermal diffusivity of liquids' and 'measuring methods and measured values', and nothing was found indicating that the said standard for comparison is not still adequate. The "Landolt-Börnstein-tables" from 1968 are edited by L. Riedel and they are results of his above-mentioned work on evaluation of the data literature concerning λ measurements begun in 1940, [22] and finished 1951, [24] (with a series of interjacent papers). In the preface to the tables Riedel says that deviations of 5% are (still) frequent although the accuracy is often given in the literature to be 1-2%, and that the values of his tables are usually values directly measured by the researchers or values smoothed out by themselves. Results have by Riedel only been combined if they agree within $\pm$ 2% which turned out to be rare. In spite of the accurate values in the tables - Riedel says - the accuracy has only in rare cases been higher than 1%.

On the basis of the above remarks the present author has concluded that his own measurements must be said to agree well with the data literature. This is most easily seen from diagrams. The Landolt-Börnstein values are therefore - after conversion of the percentages used by Riedel into normalities - only given in the diagrams. The author also concluded that his own values for solutions which are not found in the literature may be considered satisfactory contributions to the data literature.

As to the systematic errors Riedel remarks in the mentioned preface to the "L-B tables" that they may to a not negligible extent (for weakly absorbing liquids such as toluene) include thermal radiation. In [2] this source of error has only just been touched upon (loc. cit. page 9) because discussions with other investigators seemed to indicate that it is usually considered safe enough to neglect it. An investigation initiated in a work in Danish**) by the present author from 1970 has therefore not been continued.

Here it should also be mentioned that the possibility of systematic disturbances from "cross-effects" mentioned in section II of the present

*) The present work is dated March 1973, but its publication has been delayed.

**) The author's Ph. D. (lic. scient.) thesis.

work might seem to be a little pedantic. But nevertheless "cross-effects" such as the Soret-effect are in [27], Vol. 3, page 11a said to give rise to certain unresolved problems during measurements.

Since it has often been stressed in the above that it is without the scope of the present work to study existing statistical-thermodynamical theories for λ values and their agreement (for diluted solutions) with measured data, it would, maybe, be most rational not to try any curve-fitting in the diagrams, i.e. only to plot the values. But semiempirical and empirical proposals for λ's dependence on the concentration of electrolytic solutions are also found in the literature. As an empirical proposal it would be natural to develop λ in power series of N and to expect that higher terms in these series may be neglected when N is not too high. As a matter of fact Alas in his study of aqueous salt solutions [1] uses second-order parabolae for fitting, but it is found in all his cases that in the N-interval investigated in the present work ($0 \leq N \leq 2$) the curvature is negligible. Furthermore Riedel says in the mentioned preface to his "L-B tables" that λ for inorganic acids and salts - in concentrations that are not too high - depends (almost) linearly on the molarity. It is also remarkable how well the values recommended by him, and given in the diagrams above, fit with straight lines through the point $(10\lambda, N) = (6.00, 0)$ - or strictly speaking (5.99, 0) since Riedel considers the value $\lambda = 0.599$ W m^{-1} ^{o}C^{-1} the most reliable for pure water at room temperature. The present author initially chose 0.600 W m^{-1} ^{o}C^{-1} and has stuck to it because that deviation is of no importance.

In accordance with the remarks immediately above the λ values measured with the full automatic set-up have been smoothed out by straight lines in the diagrams, and these lines have been drawn through the points $(10\lambda, N) = (6.00, 0)$. This is in disagreement with the adjustment of the semi-automatic measurements because, when these were plotted in [3], the "calibration-point" ($N = 0$) was considered as obtained by a measurement on a par with the λ measurements themselves (and it was ignored that, strictly speaking, the calibrations ought to be ascribed higher weights, because they were carried out using more individual measurements than at the λ determinations). But now the following viewpoint has been preferred: Usually one has in a situation like the present one a theory or a hypothesis which one wants to test. If the series of experiments had been planned with that purpose, careful statistical tests (using regression lines) should have been possible. However, the present work has been planned as a work on a measurement technique and its theory (giving also certain contributions to the data literature). According to the above it is therefore considered per-

missible to present the results smoothed out in accordance with the "empirical hypothesis"

$$\left.\begin{array}{l} \lambda = \alpha N + \beta \\ \alpha = \text{const} \\ \beta = \text{const} \\ T = \text{const} \\ 0 < N \leq 2 \end{array}\right\} \qquad (19)$$

and to let the diagrams alone indicate the agreement. In (19) β is equal to λ_{H_2O}, and seen from this viewpoint the smoothing-out lines should be drawn through $(\lambda,\ N) = (\lambda_{H_2O},\ 0)$. If (19) should be tested by regression analysis much fewer solutions should have been measured on, each at much more different concentrations within the time at disposal.

As the experiments have been carried out mainly with only 4 or 5 determinations in the chosen N interval, there seems to be no difference of any real importance between the two ways of smoothing-out mentioned above.

If (19) is accepted, β at room temperature is known almost exactly and it is easy to estimate the standard deviation of α. The straight lines have been found graphically and they must be expected to correspond to a least-squares fit. This gives

$$\alpha = \frac{n\Sigma N\lambda - \Sigma N \cdot \Sigma\lambda}{n\Sigma N^2 - (\Sigma N)^2} \ ,$$

where n = the number of measurements for which, at the full automatic measurements, $N > 0$ and 'Σ' refers to summation over these measurements. For the standard error s_α of α one has

$$s_\alpha = s_\lambda \sqrt{\frac{n}{n\Sigma N^2 - (\Sigma N)^2}} \ ,$$

where for the full automatic measurements $s_\lambda = 10^{-2}\lambda \cdot s_5 \simeq 10^{-2} \cdot 0.6 \cdot 0.2\ \mathrm{W\ m^{-1}\ K^{-1}}$, because $s_5 \simeq 0.2\%$ in the tables. As a characteristic example one may take n = 5, measurements having been carried out at the normalities $N = 0.4,\ 0.8,\ 1.2,\ 1.6,\ 2.0\ \mathrm{equil \cdot l^{-1}}$. This gives

$$s_\alpha \simeq 5 \cdot 10^{-4}\ \mathrm{W\ m^{-1}\ K^{-1}}.$$

The straight lines representing the smoothing-out of Riedel's and own measurements respectively agree well, but it is remarkable that in <u>all</u> cases slightly lower

λ values are read from those first mentioned. This is the reason why the author considers it probable that the systematic errors of his measurements make the results (slightly) too high.

Concerning the present investigation as a whole the following should finally be remarked. There are three aspects that might be expected to be included. 1) The modified method should also be applicable to dielectric liquids. 2) It should of course also be applicable at other temperatures than room temperature, and 3) for predictive purposes one often defines "the molar λ depression" and considers that quantity as composed additively of independent contributions from the ions of the electrolyte. The validity of this rule can be investigated on the basis of λ value tables.

As to 1) and 2) these points were investigated in a few cases, but practical circumstances at the research establishment made it necessary to close down the work before they could be studied systematically. Concerning 1) it should therefore only be mentioned that a few measurements were made on ethyl alcohol, glycerol, and carbon tetra chloride and found*) "in good agreement with the data literature". Concerning 2): 5 individual electrolytic solutions chosen at random were measured on at elevated temperatures (up until 60°C), and it was found that the values agreed as well with Riedel's "Landolt-Börnstein values" as did the measured values at room temperature in cases where "L-B values" could be found. Furthermore they all agreed with the rules Riedel gives for computing λ for not too highly concentrated solutions at one temperature when it is known at another. These rules are given in the preface to Riedel's L-B tables.

The investigations concerning 1) and 2) were considered too unsystematical to be mentioned in detail. To delve into the problem 3) is interesting. Thus Eigen [9] has given a theoretical background for the rule of the "independent ion-contributions". But as a matter of fact it can - seen from an empirical point of view - hardly be said to be more than a rule with many exceptions. Salts like NaF and Na_2CO_3 show negative depression, which does not make the rule invalid, but it is remarkable that so "ordinary" electrolytes as K_2CO_3, NaOH, and KOH show anomalies (according to Riedel's express statements in his above-mentioned preface). 3) has therefore not been discussed in further detail in the present work, the scope of which has been delimited in the present section.

*) The measurements were performed with the semiautomatic device (i.e. with "small accuracy").

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The author is greatly indebted to Professor, dr.phil. T. Bjerge, former director of Risø, for his permission to start the work reported in [2] and [3] (the author's Ph.D. thesis). Dr.techn. J. Marstrand showed a stimulating interest throughout the work on the project, and the author further wishes to acknowledge the kind assistance of numerous colleagues whose names have been mentioned at the appropriate places in the body of the paper.

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The above list comprises only works to which has been directly referred in the present work. In the works [2], [3], and [4] by the present author, which are abstracted here since they constitute the foundations of the investigations set forth, reference has furthermore been made to the following literature:

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I. Purpose and Contents of the Present and Earlier, Relevant Works by the Author

During the last decades the transient hot-wire method has been increasingly used as a method for measurement of the thermal conductivity λ of liquids. Briefly, its principle is as follows. The liquid is filled into a cylindric cell vertically placed in a thermostat. Along the axis of the cell a hot wire is located. If an electric current is fed into a circuit of which the cell is a component, heat will flow from the wire into the liquid. The better the liquid conducts the heat away from the wire, the more slowly the wire temperature increases. In addition to its function as a source of heat, the wire therefore acts, in most designs, as a resistance thermometer, which makes it possible to register its temperature versus time curve by means of a recorder built into the circuit. The wire temperature can also be measured by means of a thermocouple. From the curve registered, and from certain other measurements in the system, the thermal conductivity of the liquid can be deduced according to the theory of the method.

In this and the following section is given a brief survey of earlier works by the author [2] , [3] , [4] on the method. The "classical" field of application of it is pure, dielectric liquids. The main result of the said works is a new modification of the method to comprise also electrolytic solutions.

In spite of the fact that certain advantages are often claimed for the method, such as those of being "elegant", fast, and convenient, amazingly few attempts have been made to expand it for measurements on electrolytic solutions since it was introduced in 1931 by Stålhane and Pyk [26] and refined in 1938 by Eucken and Englert [11]. In [3], page 5, are mentioned 2 published works on such an expansion, [29] by van der Held et al. from 1949 and [1] by Alas from 1967. In these works the expansion is carried out by surrounding the hot wire with an electrically insulating coating. Furthermore, quotations are given in [3], page 6, which show that in the literature on the method it is always understood - tacitly or explicitly - that this is the only possibility of making the method applicable to electrolytic solutions.

However, for various reasons it would be desirable to avoid the insulation: In [3], page 32, some theoretical complications owing to the coating are given. To avoid these complications it is necessary to use an extremely thin insulating layer. This is done by Alas [1], but he did not succeed in finding an insulation material usable at all pH values. His insu-